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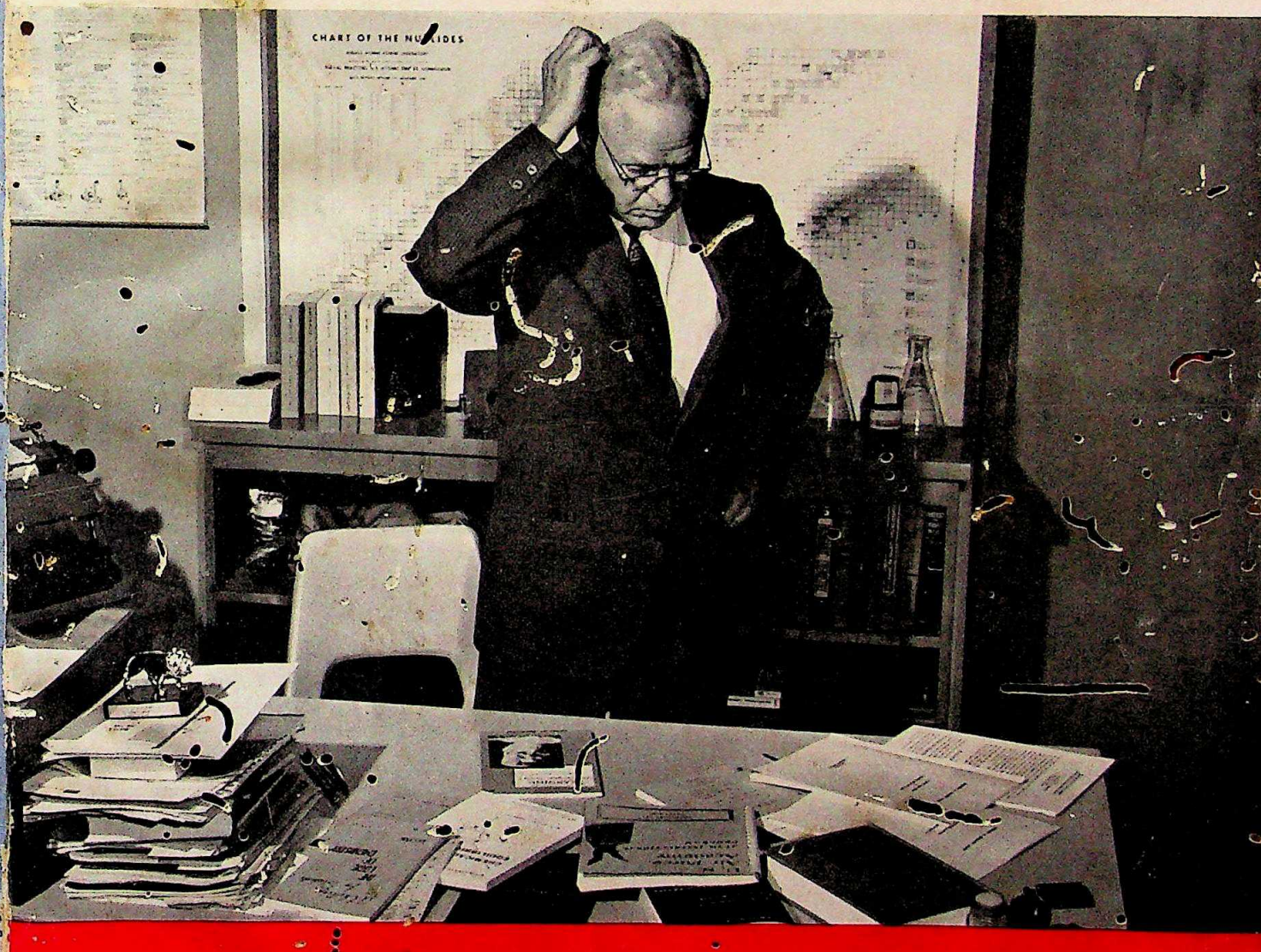
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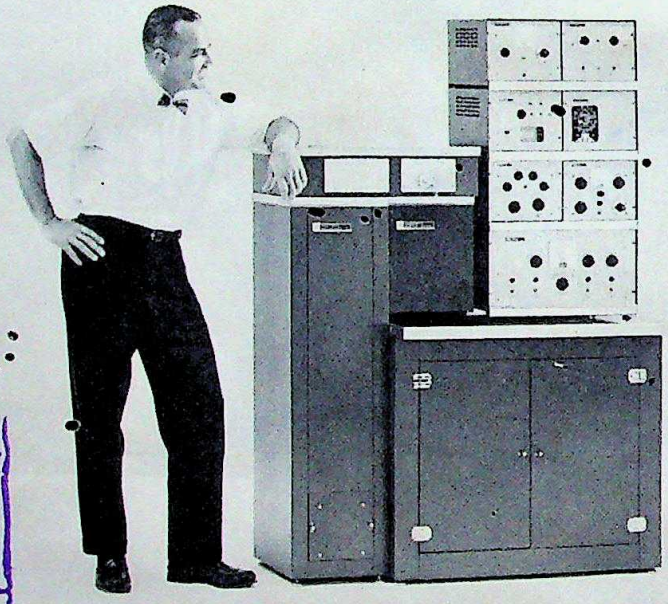
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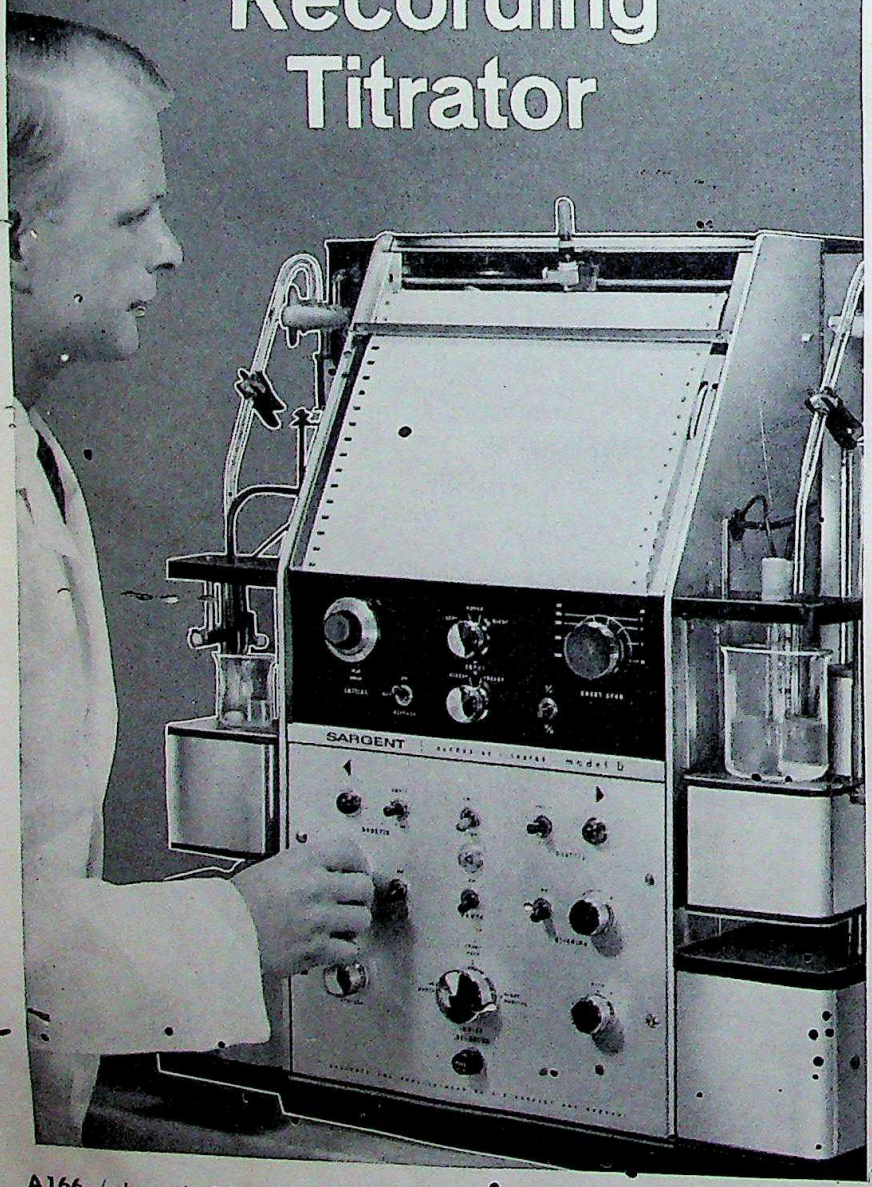
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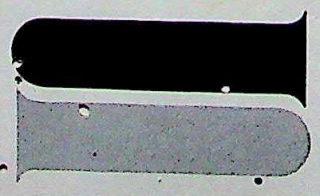
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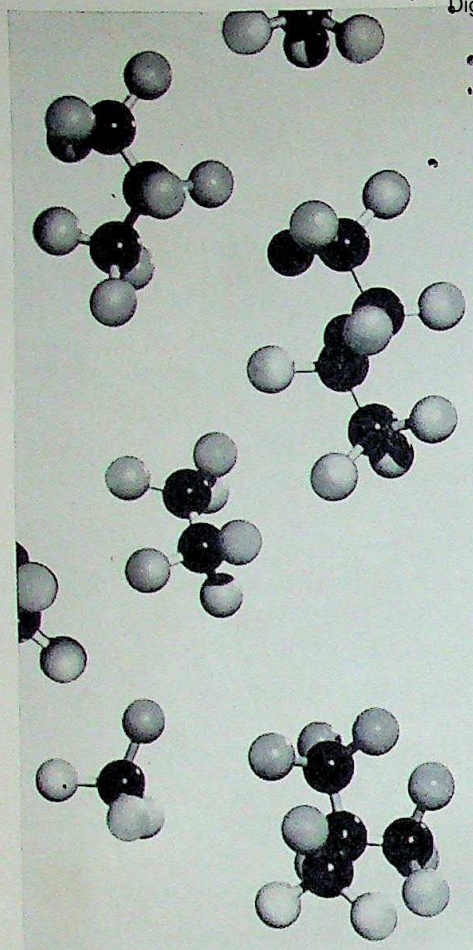
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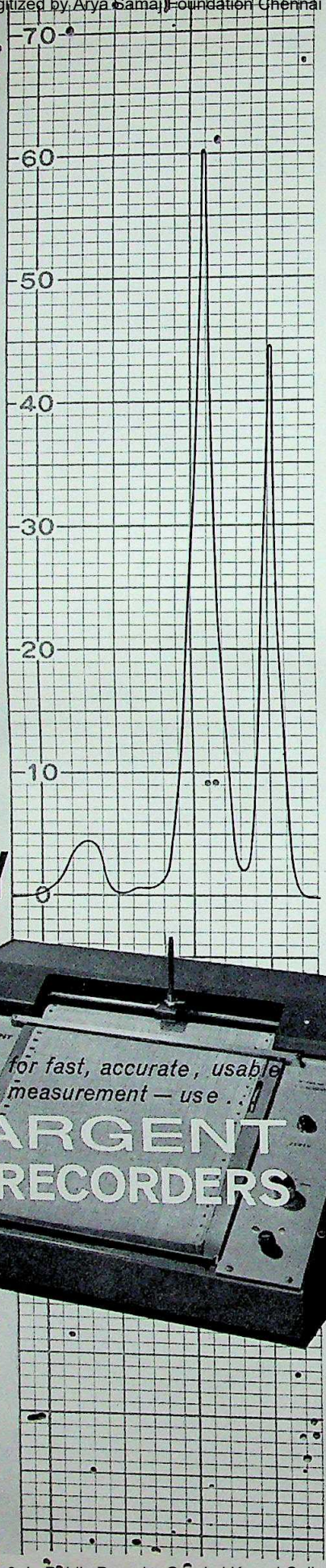
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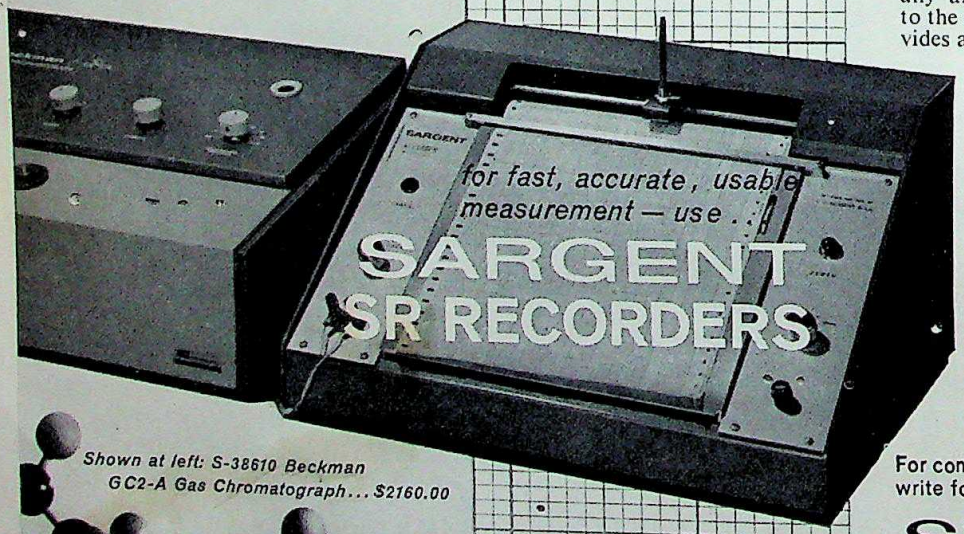
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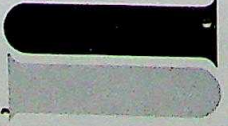
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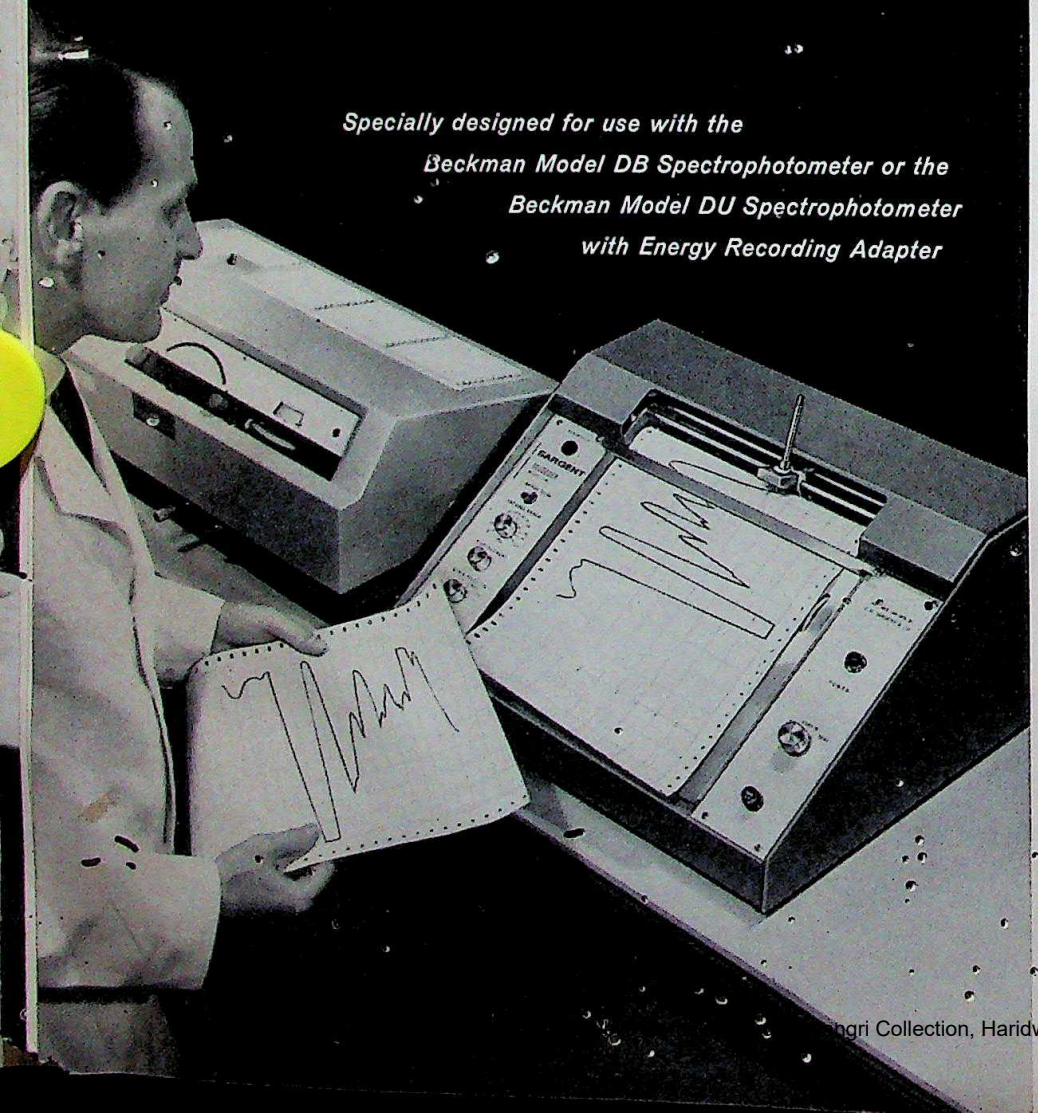
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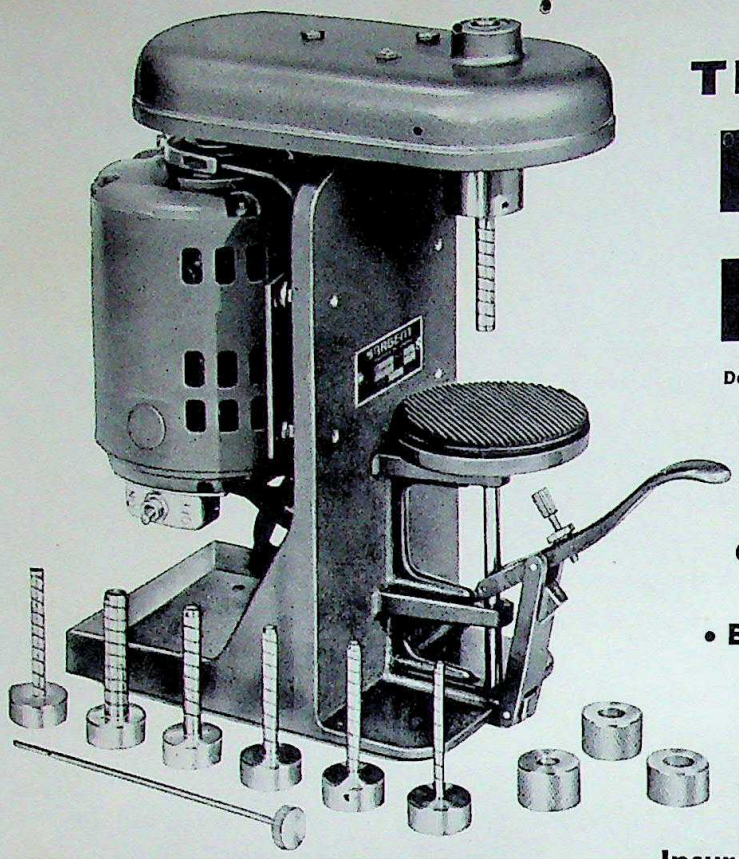
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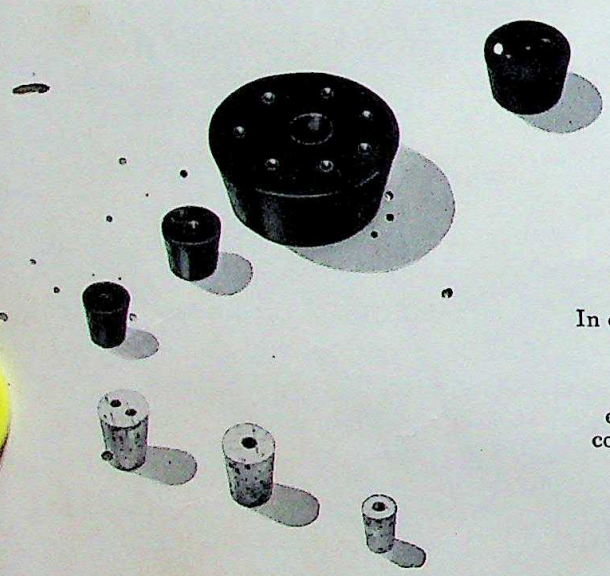
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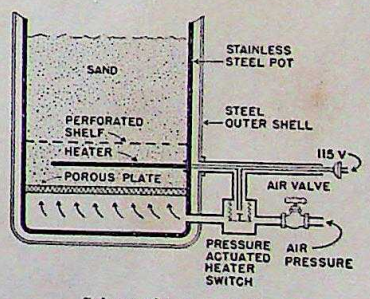
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Topics in . . . **Chemical Instrumentation** . . . a ChemEd feature

Edited by **S. Z. LEWIN,** New York University, New York 3, N. Y.

These articles, most of which are to be contributed by guest authors, are intended to serve the readers of this JOURNAL *by calling attention to new developments in the theory, design, or availability of chemical laboratory instrumentation, or by presenting useful insights and explanations of topics that are of practical importance to those who use, or teach the use of, modern instrumentation and instrumental techniques.*

V. Thermometric Titrators

Joseph Jordan, *Department of Chemistry, The Pennsylvania State University*



Joseph Jordan obtained his Ph.D. degree in 1945 at the Hebrew University, Jerusalem, Israel. He came to the U.S. in 1950, served as Research Fellow and Instructor at Harvard and at the University of Minnesota, and in 1954 joined the faculty of The Pennsylvania State University where he is now Professor of Chemistry. Dr. Jordan teaches analytical chemistry on the undergraduate and graduate levels. He conducts research in the electrochemistry and thermochemistry of aqueous solutions and fused salts. He is a member of the International Commission on Electrochemical Thermodynamics and Kinetics, affiliated with the International Union of Pure and Applied Chemistry.

Thermometric *Enthalpy Titrations* represent the newest art in the field of instrumental analysis. Their methodological principle is based on the recording of a plot of temperature versus volume of titrant. The titrant is added to an isothermal (*titrate* = solution titrated) in an adiabatic *titration calorimeter*. In most instances, a change in enthalpy occurs concomitantly, yielding a corresponding heat of reaction. As a result, titration curves (called *enthalpograms*), of the shapes shown in Figure 1, are generally obtained.

Curves I and II illustrate an exothermic and an endothermic *titration reaction*, respectively. On both enthalpograms the *base lines* AB represent *temperature-time blanks*, recorded prior to the start of the actual titration. B corresponds to the beginning of addition of titrant, C is the end point and CD the excess reagent line. BC is the *titration branch* proper of the enthalpograms: It has an ascending slope when $\Delta H < 0$, and a descending slope when $\Delta H > 0$. In Figure 1 the *excess reagent branches* of the enthalpograms (CD) were drawn with ascending slopes, because the dilution of most titrants is an exothermic process. In order to minimize variations in heat capacity during titrations, it is customary to use titrants 50–100 times more concentrated than the "unknowns" titrated. Thus the volume of the titrate solutions is maintained virtually constant, but the titrants are diluted appreciably. The heats of dilution can be corrected for conveniently by the linear back extrapolation CB′ (see Figure 1). Under these conditions, the *extrapolated ordinate heights*, BB′, represent a measure of the change of temperature, ΔT, due to the titration reaction, as well as of the integral heat, Q, evolved or absorbed, viz.:

$$\mathrm{BB}' \; prop \; \Delta T = \frac{Q}{k} = \frac{-N \cdot \Delta H}{k} \qquad (1)$$

where k denotes the effective heat capacity and N is the number of moles reacted in the titration. It is evident from equation (1) that the quantity BB′ (appropriately calibrated) can be used for obtaining the following types of information:

a. The heat of the titration reaction, ΔH, whenever a known amount of titrate is used.

b. The concentration of an unknown titrate, whenever ΔH is known (ΔT is proportional to concentration and independent of titrate sample size, because—in a given titrate solution—both N and k are proportional to the sample volume).

c. The quantity of an unknown in a known volume of titrate.

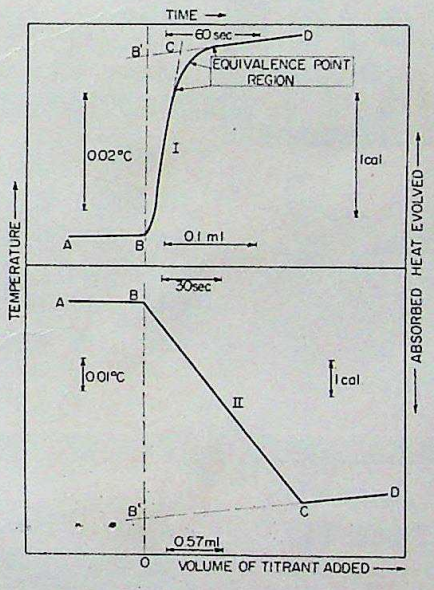


Figure 1. Typical Enthalpograms.

I. Example of exothermic titration reaction: 0.0009 molal potassium chloride titrated with 1.4 molal silver nitrate in a molten $LiNO_3$-KNO_3 eutectic solvent at 158°C, yielding sparingly soluble AgCl(s).

II. Example of Endothermic Titration Reaction: 0.014M magnesium chloride titrated with 1M ethylenediaminetetraacetate (Y^{4-}) in aqueous solution at 25°C, yielding the chelate $[MgY]^{--}$.

AB. Temperature-time blank (base line), recorded prior to start of titration

B. Start of titration

C. End point

CD. Excess reagent line

Approach *a* is ideally suited for the rapid and convenient determination of heats of reaction in dilute solutions. *B* and *c* can be applied to a unique type of *direct enthalpimetric analysis* which does not require a standardized titrant. A more precise application of enthalpograms to quantitative analysis is inherent in the conventional *end point determinative technique*, to calculate the amount of an unknown in the titrate from the volume of an accurately standardized titrant required to attain the equivalence point. Naturally, the stoichiometry of the titration reaction must be known for this. Conversely, unknown reaction stoichiometries can be determined using known amounts and/or concentrations of both titrant and titrate. In instances, when the titration reaction is appreciably incomplete in the equivalence point region (e.g., Figure 1, Curve I), the enthalpograms exhibit a curvature from which the equilibrium constant (and the corresponding standard free energy) can be estimated.

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Combining this with the reaction heat which is independently accessible from any enthalpogram, the entropy can readily be calculated from the well-known equation:

$$\Delta S^\circ = \frac{\Delta H^\circ - \Delta F^\circ}{T} = \frac{\Delta H^\circ + RT \ln K}{T} \qquad (2)$$

Thus all three important thermodynamic parameters of the titration process (viz. the heat, ΔH°; the free energy, ΔF°; and the entropy, ΔS°) can be obtained *from one single experiment*, which is an accomplishment unmatched by any other method. The nature of the information accessible from the judicious mathematical analysis of thermometric titration curves is summarized in Table I.

Nomenclature

Operationally, for the majority of "thermometric" titration curves, the experimental variable monitored being temperature. The basic property which determines their shape is enthalpy change. This accounts for the designations "thermometric titration" and "enthalpy titration" used by various authors. Other terms encountered in the literature for naming similar procedures include: "calorimetric titration," "thermochemical titration," "thermal titration." Growing interest in thermoanalytical titrimetry led in 1957 to the scheduling of a symposium at the Fall Meeting of the American Chemical Society in New York City. The program included a round-table discussion on terminology. The consensus was that the designation "thermometric titration" be preferred in keeping with accepted usage for potentiometric, amperometric, etc., techniques.

Table I. Synopsis of Applications of Thermometric Titrations

Information obtainable		Procedure for calculating data from enthalpograms
Analytical applications	Concentration of an unknown	Direct enthalpimetric
	Amount of an unknown	End point determinative
Fundamental applications	Heat of reaction	From extrapolated ordinate heights
	Free energy of reaction	From curvature in equivalence point region
	Entropy of reaction	From equation 2
	Reaction stoichiometry	End point determinative

Instrumentation

Thermometric titration has been reported as early as 1913: It was carried out by a discontinuous procedure, adding increments of 0.1 M ammonium hydroxide from a conventional volumetric buret to a 0.1 M solution of citric acid in a Dewar flask. After each addition of titrant a corresponding temperature reading was taken from a Beckman thermometer, immersed in the titration cell. The shape of such manual enthalpograms was poorly reproducible. Temperature changes were relatively large (up to several degrees C) and it was necessary to wait 5–10 minutes before taking each temperature reading, due to the slow response and appreciable heat capacity of the mercury thermometer. A complete titration required about an hour. Heat exchange with the laboratory environment was inevitable, with the result that the titration curves obtained depended somewhat on the patience of each experimenter. This unsatisfactory situation was remedied in the fifties with the invention of automatic thermometric titrators using semiconductor instrumentation and electrically powered continuous constant flow burets. With these devices it has become possible to titrate extremely dilute solutions (10^{-4} to 10^{-2} M), to minimize temperature changes to <0.1°C., to reduce the time required for an entire titration to five minutes or less and to eliminate human error entirely. With the advent of automatic instrumentation, thermometric titrimetry has been transformed into an important quantitative

(*Continued on page A8*)

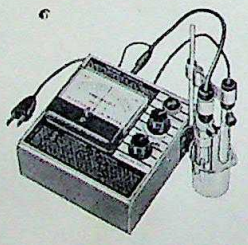
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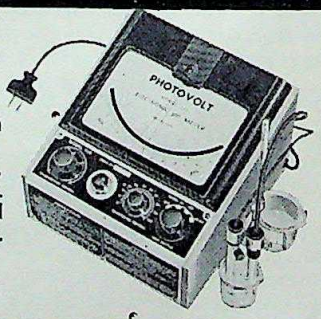
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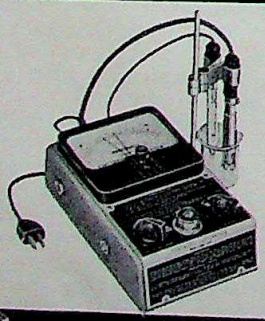


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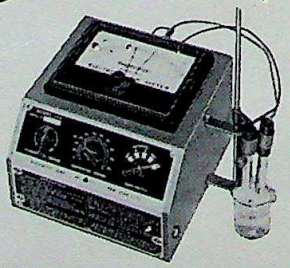




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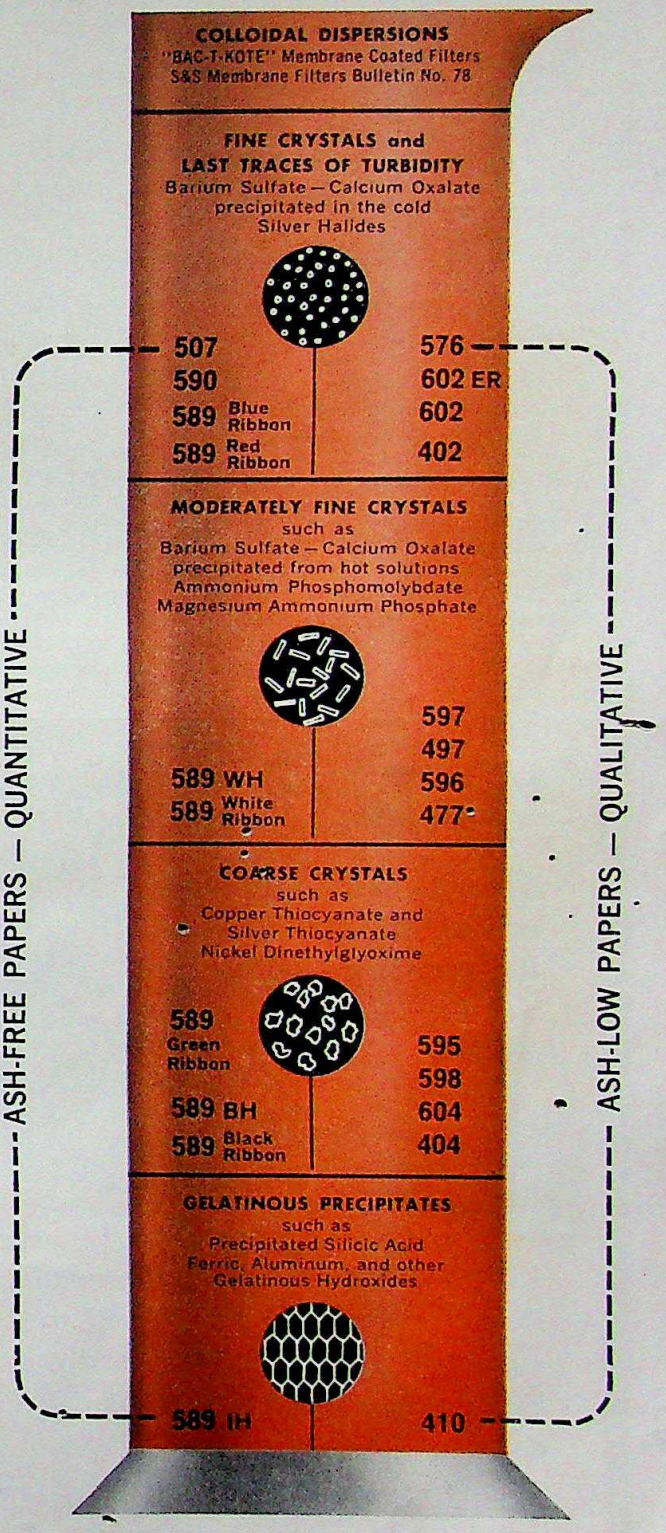
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method: This is an interesting instance where *instrumentation represents not merely a convenience, but a methodological necessity.* Use of an instantaneous electric signal for monitoring temperature is an absolute requirement for eliminating the irreproducibility which has haunted the manual thermometric titration techniques of yesteryear.

The major breakthrough which has made possible automation of thermometric titrations was accomplished in 1953 by Linde, Rogers, and Hume at MIT. They adopted as the temperature sensing device semiconductors known in the USA as "thermistors," and in Western Europe as *NTC-s* (= *N*egative *T*emperature *C*oefficient).[1] In 1956 an automatic titrator equipped with a motor driven syringe-buret was developed at The Pennsylvania State University. Finally, in February, 1962, the first commercially manufactured automatic thermochemical titration instrument, trade-named the *Titra-Thermo-Mat*, was made available by the American Instrument Company (AMINCO), Silver Spring, Maryland.

[1] Suppliers from whom thermistors can be obtained include: Victory Engineering Corporation (VECO), P.O. Box 373, Union, N.J.; Fenwal Electronics, Inc., Framingham, Mass.; The General Electric Co., Metallurgical Products Department, Detroit 32, Mich.; and Yellow Springs Instrument Co., Inc., Yellow Springs, O.

The key to automatic thermometric titration instruments is the thermistor. This is a solid state device, made of sintered metallic oxides. In thermometric titrators, it is used in the shape of a small bead (<1 mm in diameter), covered by a thin glass envelope, and is wired as one arm of a DC Wheatstone bridge. A block-diagram of a typical home-made thermistor-titrator is shown in Figure 2. Thermistors function as highly sensitive resistance thermometers:

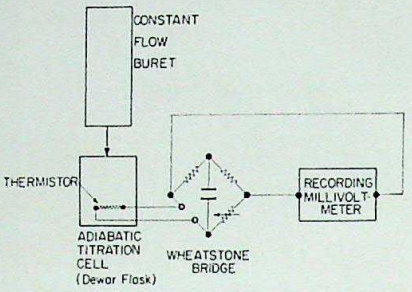


Figure 2. Block diagram of "home-made" automatic thermometric titrator.

In contradistinction to metals, thermistors possess large *negative* temperature coefficients of resistance, as is illustrated in Figure 3.

As can be seen in the figure, the resistance of platinum increases slightly with temperature: This is due to the fact that in metals, the "effective concentration" of electrons available for conduction is the same irrespective of temperature, but their mobility is decreased by enhanced thermal

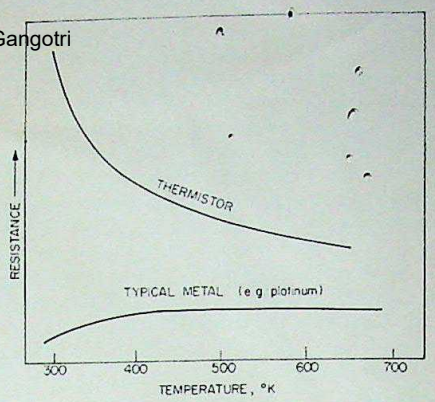


Figure 3. Plots of resistance as a function temperature.

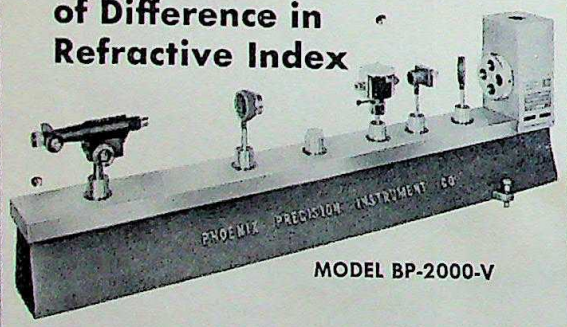
fluctuations of the atomic nuclei. The resistance of thermistors decreases drastically with temperature, because these semiconductors possess a conduction band, separated from the valence band by an energy gap of the order of κT: As the temperature increases electrons are transferred to the conduction band and resistance decreases accordingly.

Within small temperature intervals (up to 1°C) the unbalance potential of a thermistor bridge represents a linear measure of temperature. Typical performance characteristics of thermistors include: Negligible heat capacity; negligible power dissipation; response lag <1 sec; resistance at 25°C — 2000 ohm; temperature coefficient −0.04 ohm/ohm/degree. A thermistor, wired as illustrated

(*Continued on page A10*)

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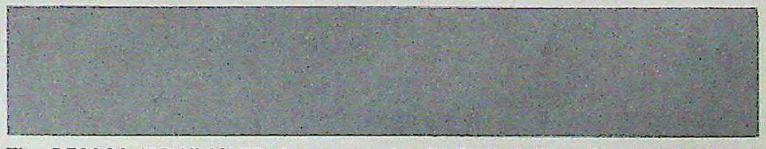
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in Figure 2, produces an unbalance potential on the order of 40 millivolt per degree C, which is equivalent to the response of a two thousand junction thermocouple.

Most thermometric titrators are designed to record automatically "normal" enthalpograms, i.e., plots of temperature *versus* volume of titrant. Their operating principles and performance characteristics are discussed in detail below as exemplified in the Titra-Thermo-mat. Specialized instruments have been constructed in various laboratories for recording differential and derivative thermometric titra- are referred to the appropriate references in the bibliography.

The Titra-Thermo-Mat

A self-explanatory photograph of the Titra-Thermo-Mat is shown in Figure 4.

It consists essentially of: (a) The *Menisco-Matic* Buret; (b) An "adiabatic titration tower"; (c) A thermistor bridge assembly; (d) A recording DC millivoltmeter.

Components *a*, *b*, *c* are assembled in one vertical unit, seen on the left of photograph (*a* is at the top, *c* is in the base of the instrument). *D* is at the right and displays two titration curves of hydrochloric acid with standard sodium hydroxide.

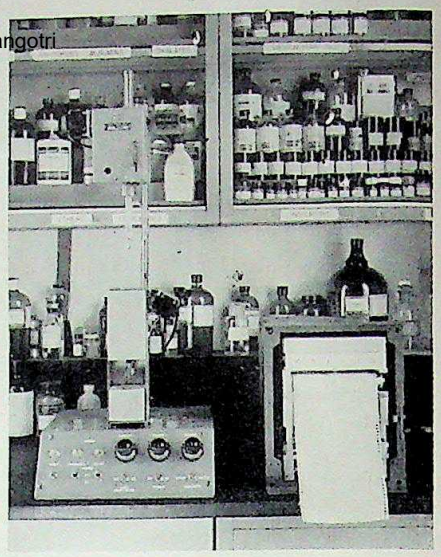


Figure 4. The Aminco TITRA-THERMO-MAT; adiabatic titration tower in loading position.

The Menisco-Matic Buret is equipped with a precision machined Vycor plunger, coupled with a screw which is driven by a synchronous motor at constant speed. As the plunger advances, it displaces a volume of titrant at a rate of 600 microliters/minute. The titrant reservoir is made of Pyrex: Embedded in it is a thermistor which can be connected to the Wheatstone bridge for measuring the temperature of the titrant, if desired. Details of the buret are shown in Figure 5, including a digital counter which provides direct readout of the volume of titrant dispensed.

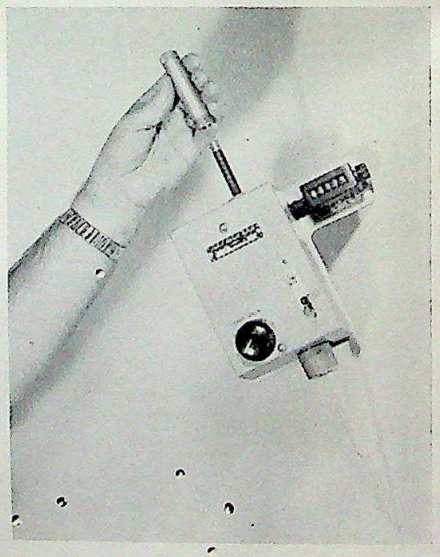
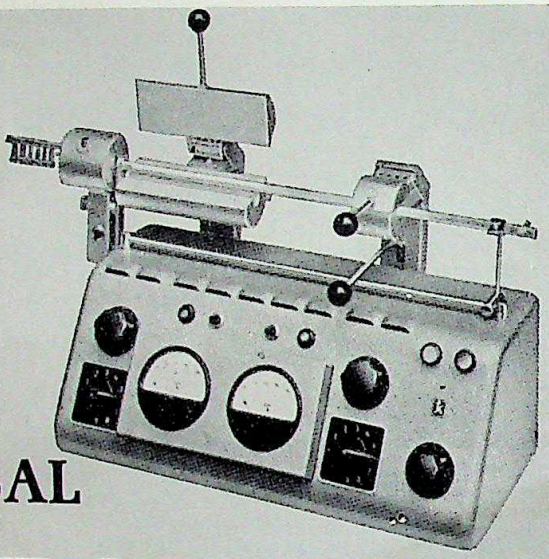


Figure 5. Aminco MENISCO-MATIC BURET.

The "adiabatic titration tower" is shown in a loading position in Figure 4, and in its "titration position" in the cross-sectional line drawing in Figure 6. The tower is made of Styrofoam plastic which serves as thermal insulator. Its lower section contains a 30 ml sample beaker into which the titrate solution is placed. In the "titration position" the beaker is raised to immerse into it the buret tip, a small L-shaped heater, a stirrer, and a "sample" thermistor. The heater can be used as a calibrating device for determining heats of reaction.

Either the sample thermistor or the

(*Continued on page A12*)



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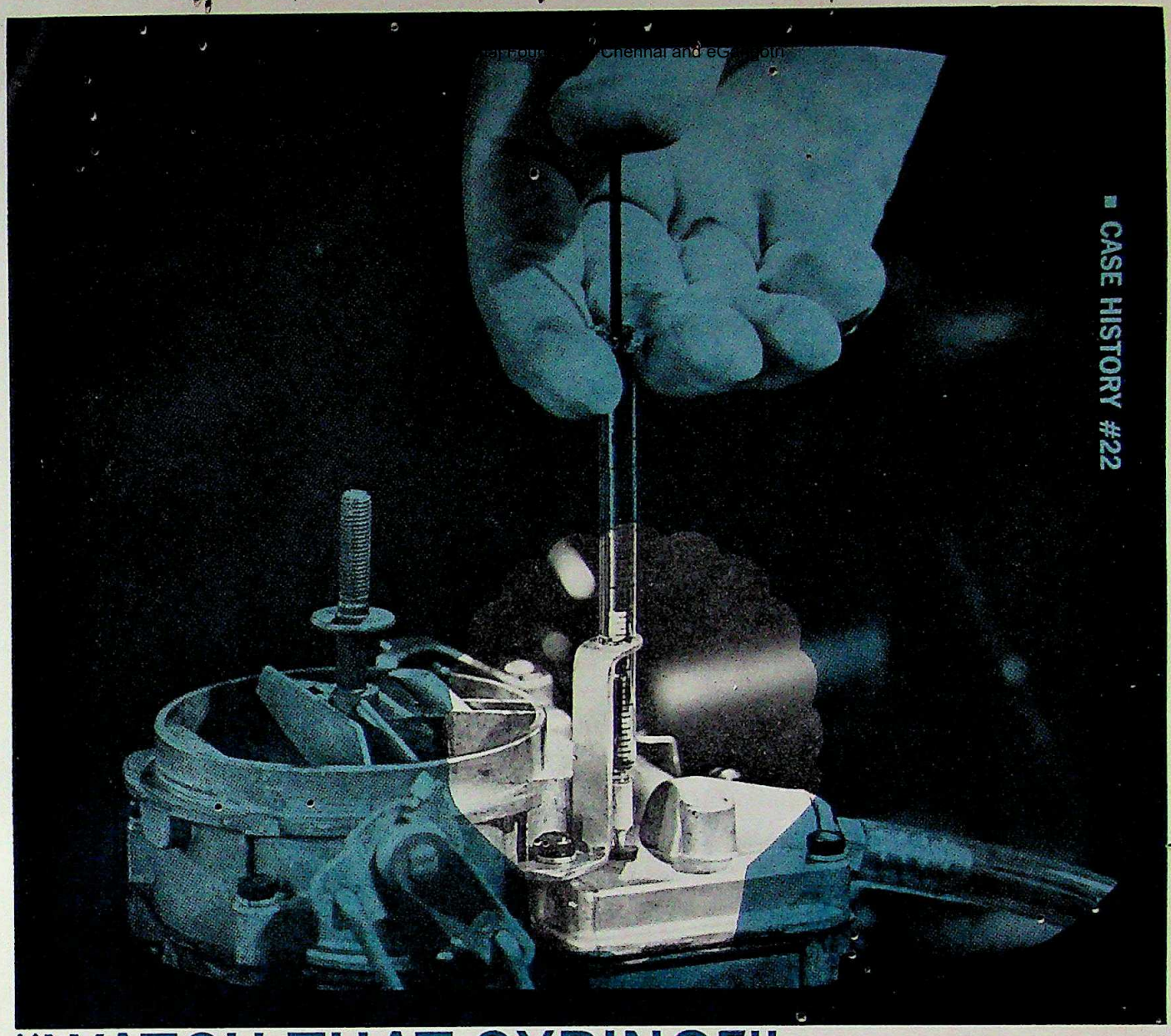
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titrant thermistor can be connected as an arm of the Wheatstone bridge, by a selector switch: If the sample solution is colder than the titrant, it may be warmed up with the aid of the heater. Generally titrant and titrate temperatures should be within 0.2°C. When performing a titration, a "base line" is first obtained on the recorder by adjusting the two balance dials on the instrument panel. The sensitivity dial, which controls the bridge input voltage, is adjusted and the titration is carried out with the thermistor selector switch in the "beaker (= sample) position." On the recorder chart, the ordinate deflection is proportional to change in temperature. The abscissa is proportional to volume of titrant, because the chart is driven by a synchronous motor at a constant rate, as is the Menisco-Matic Buret.

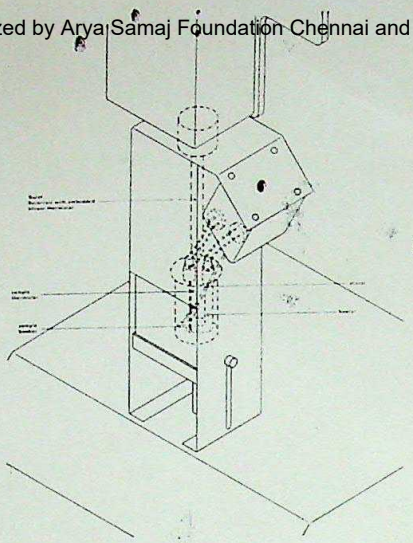


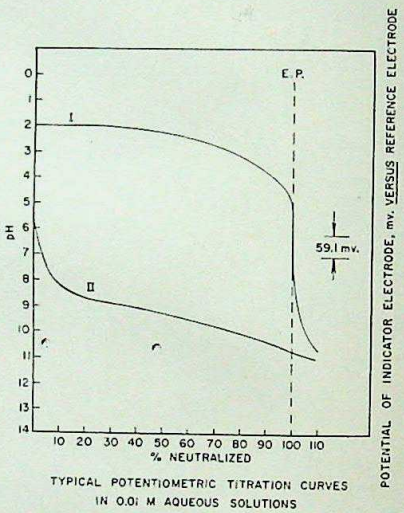
Figure 6. Adiabatic tower in titration position.

Unique Features and Significance of Thermometric Titrations

Most analytical procedures are ultimately "free energy methods," i.e., they depend on a property related solely to equilibrium constants. For instance, the *p*H change in a conventional acid-base titration in aqueous solution depends on the relevant ionization constants. As a result, analysis of a very weak acid is not feasible by any titrimetric procedure, when the end point is determined by a conventional free-energy method (as is the case when visual color indicators or potentiometric titration curves are used). However, enthalpograms depend on the heat of the reaction *as a whole*, viz.:

$$\Delta H = \Delta F + T\Delta S \qquad (3)$$

Consequently, thermometric titration curves may yield a well-defined end point when all free energy methods fail, if *the entropy term in eq. 3 is favorable.*



TYPICAL POTENTIOMETRIC TITRATION CURVES IN 0.01 M AQUEOUS SOLUTIONS

I. Hydrochloric acid titrated with sodium hydroxide.
II. Boric acid titrated with sodium hydroxide.
E.P. Equivalence point.

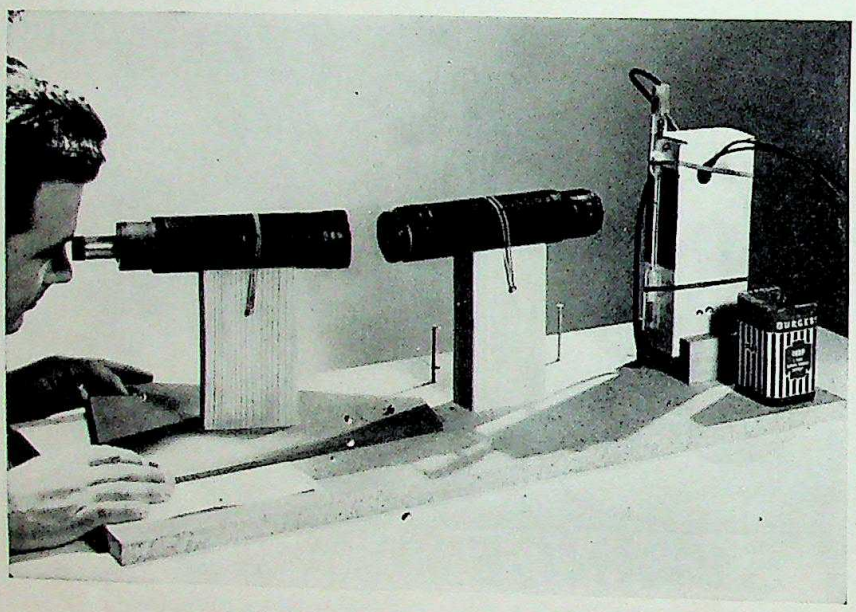
Figure 7. Potentiometric titration curves of strong and weak acids.

This is indeed the case in many alkalimetric titrations of weak acids: As an illustration, Figures 7 and 8 show potentiometric (*p*H) and thermometric titration curves of hydrochloric and boric acids with sodium hydroxide in dilute aqueous solutions. The potentiometric curves of the two acids (Figure 7) are very different yielding a large "end-point inflexion" for hydrochloric acid ($K_a \approx \infty$) and virtually none for boric acid ($K_a \approx 10^{-10}$). The corresponding enthalpograms (Figure 8) are strikingly similar, because the heats of neutralization of hydrochloric and boric acid are comparable, viz.: −13.5 and −10.2 kcal/mole, respectively. As a result the two acids can be determined with comparable ease, precision, and accuracy by thermometric titration, while any direct free energy method is bound to fail with boric acid.

Since heat of reaction is a most general property of chemical processes, thermometric titrations have a very wide range of applicability in quantitative analysis: They have been applied successfully to all important categories of "titration processes," including proton transfer (acid-

(Continued on page A14)

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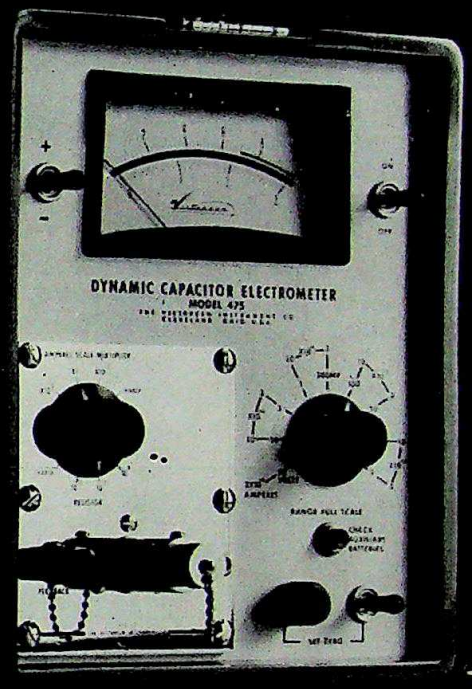
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base), oxidation-reduction and complexation reactions, in media ranging from

very virtue: Because of its general applicability, the method is non-selective.

From a fundamental point of view, thermometric titrations possess extraordinary potentialities for determining

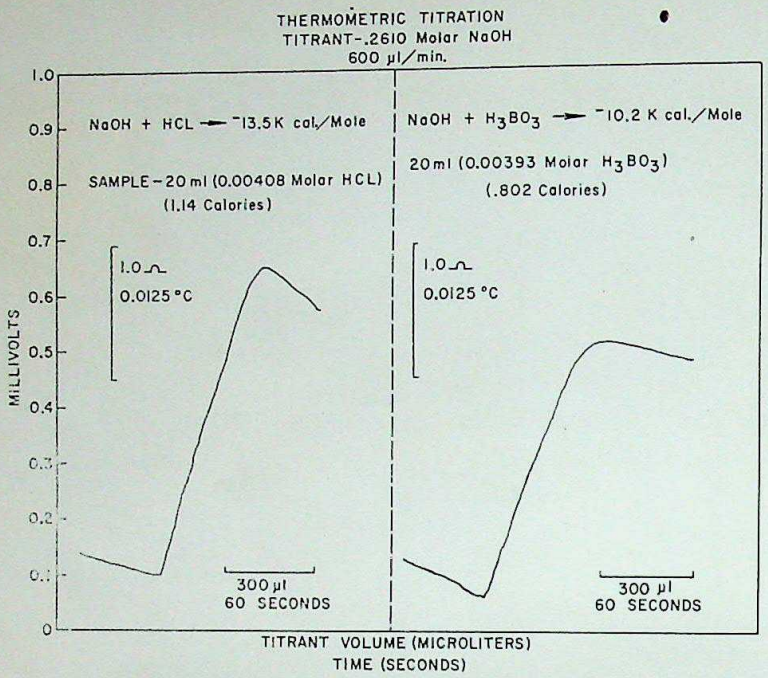


Figure 8. Thermometric titration curves of strong and weak acids.

water at room temperature to molten salts at 350°C. The main limitation of thermometric titrations is inherent in their

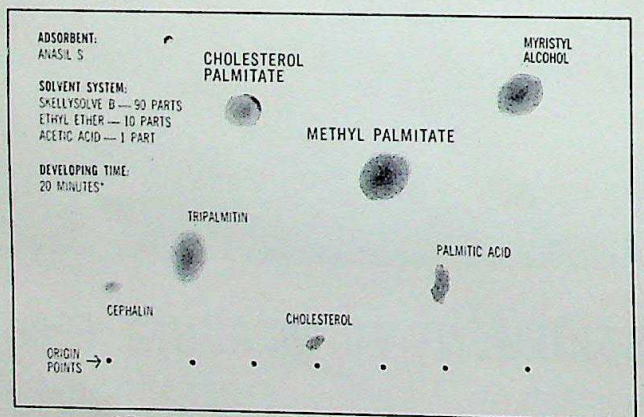
rapidly and conveniently heats of reaction in solutions so dilute that the determined

(*Continued on page A16*)

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...an output jack for use with an automatic titrator such as the Coleman Titrion.

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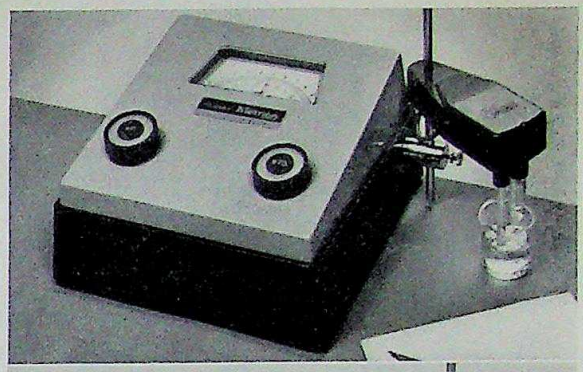
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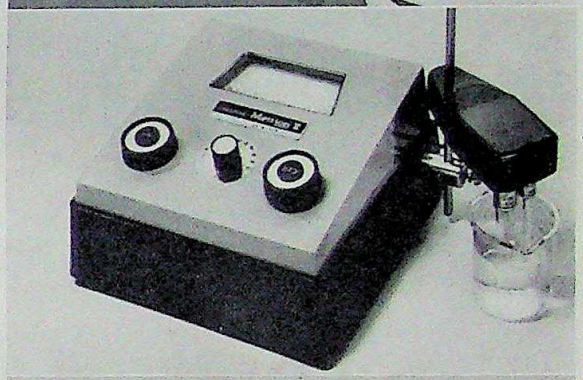
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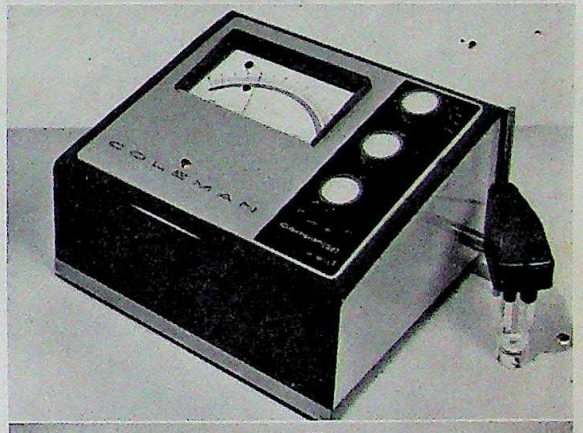
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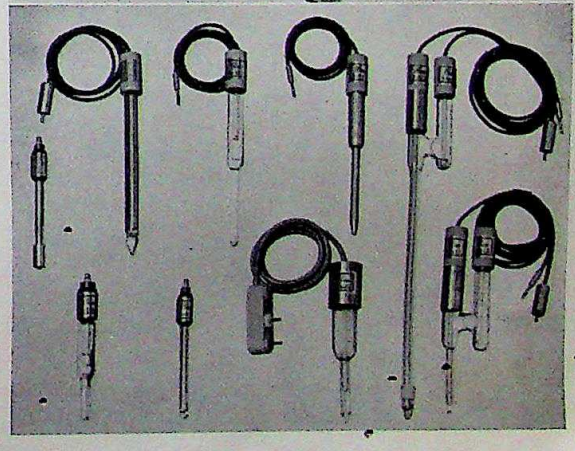
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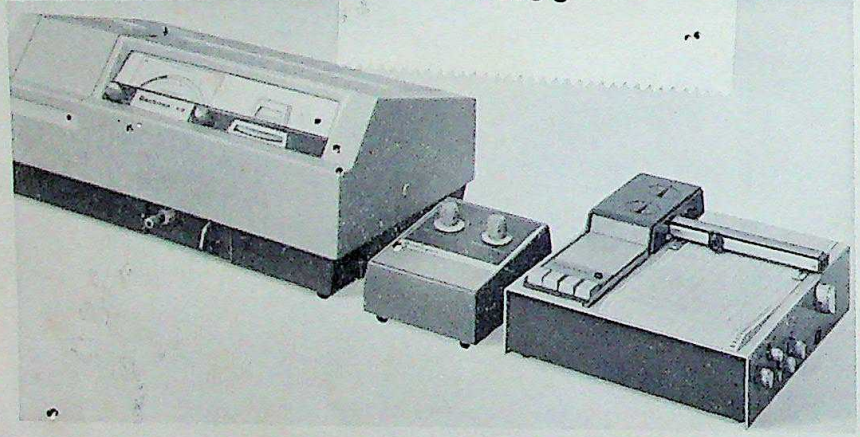
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ΔH values can be set virtually equal to the ideal thermodynamic parameters corresponding to infinite dilution. The temperature change during a titration (±0.1° or less) is so small that it can be neglected with respect to the variability of thermodynamic parameters: This is of significance in controversial situations, where an actually endothermic reaction may appear spuriously exothermic when the heat is determined by a conventional application of the Van't Hoff Isochore and averaged over temperature ranges of 50°C. Such an ambiguous situation has been recently elucidated with respect to the heat of chelation of magnesium with ethylenediaminetetraacetate, which was believed to be exothermic, but yielded the typically endothermic enthalpogram shown in Figure 1, Curve II.

Reliable thermochemical data on many important reactions occurring in solution are conspicuous by their absence, due mainly to the laboriousness of classical calorimetric procedures. Thermometric titrations can rapidly yield data on heats of reaction under specified experimental conditions. Since the free energies are readily available, this has resulted in making accessible hitherto unknown illuminating information on entropies, which in turn can serve to elucidate associative phenomena, such as ion-association and solvation, and the *detailed nature of chemical species actually prevailing in conventional solvents and molten salts.*

Thus, the analytical and fundamental applications of thermometric titrations represent two sides of the same coin. It is anticipated that the next few decades may witness advances in thermochemical methods of analysis concomitantly with progress in the understanding of the nature of "entropy compounds." This would parallel the spectacular development of electroanalytical chemistry during the past several decades which has lead to tremendous advances in the knowledge of kinetics and mechanisms of electrode reactions.

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(*Continued on page A21*)

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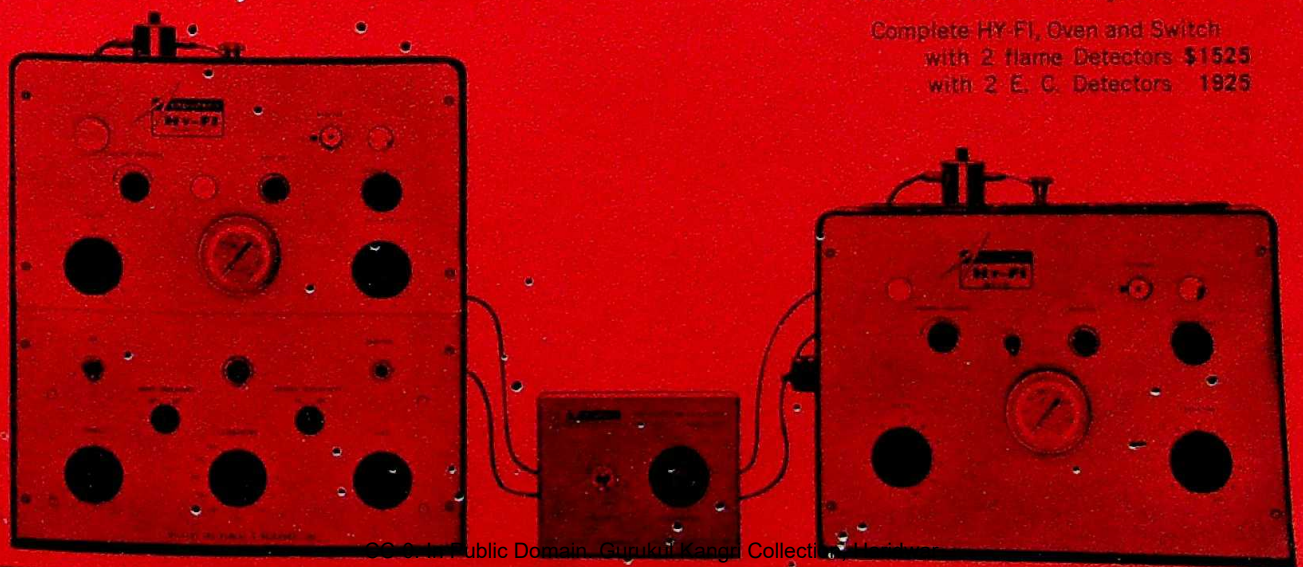
was the comment by one petroleum research chemist who uses the Hy-FI. He had just cooled the Hy-FI oven to -50°C with dry ice, and programmed it to 380°C in a wide-spectra analysis C_1 to C_{37}.

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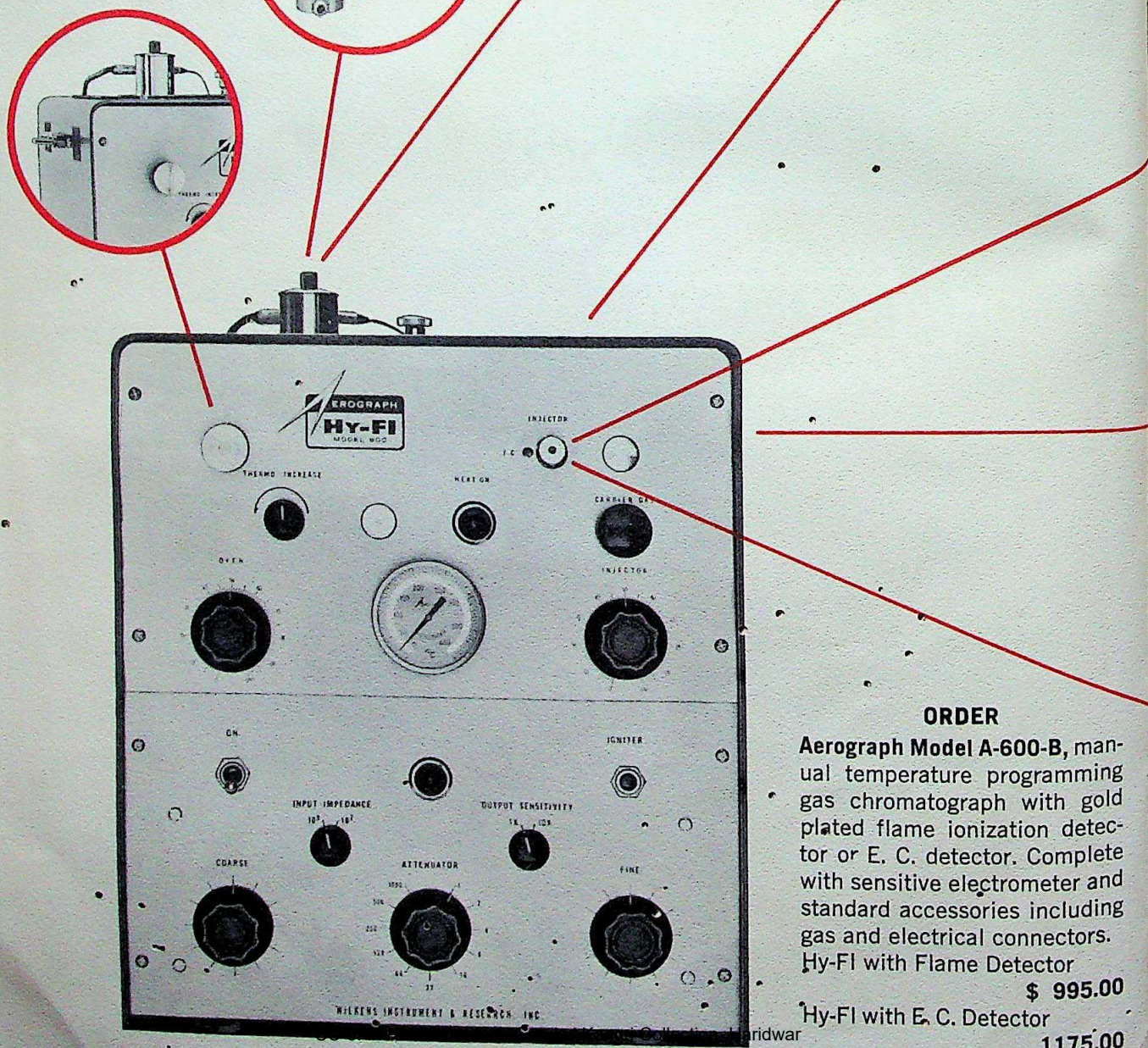
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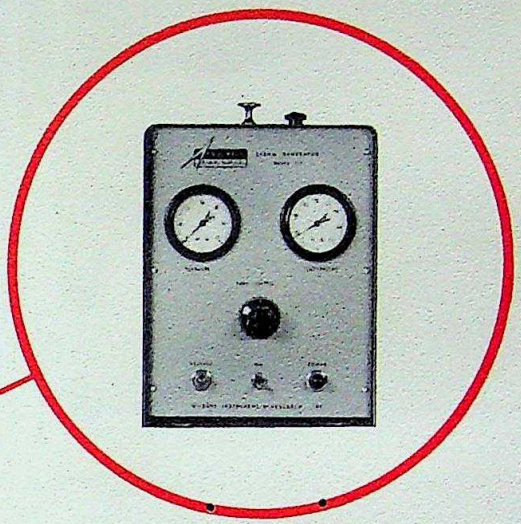
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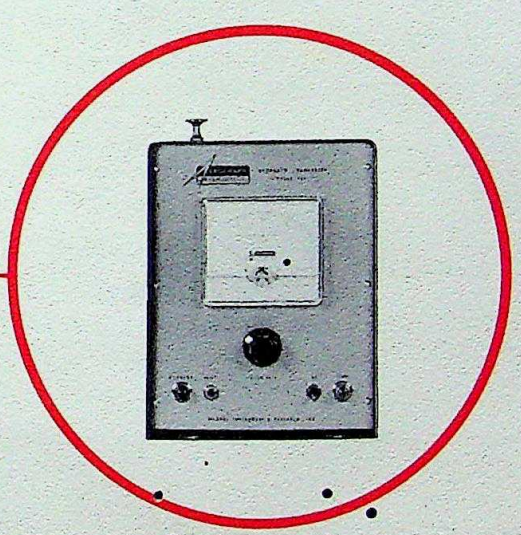
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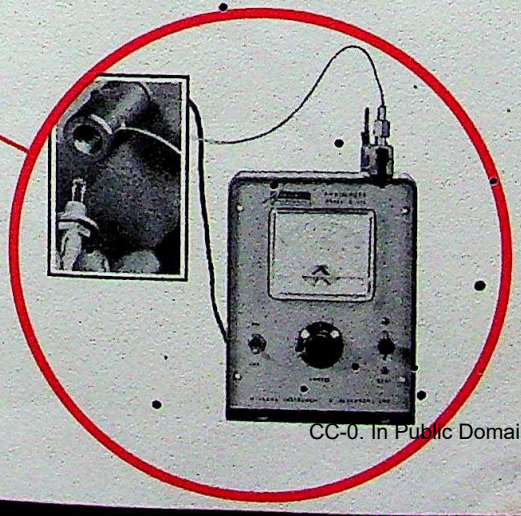
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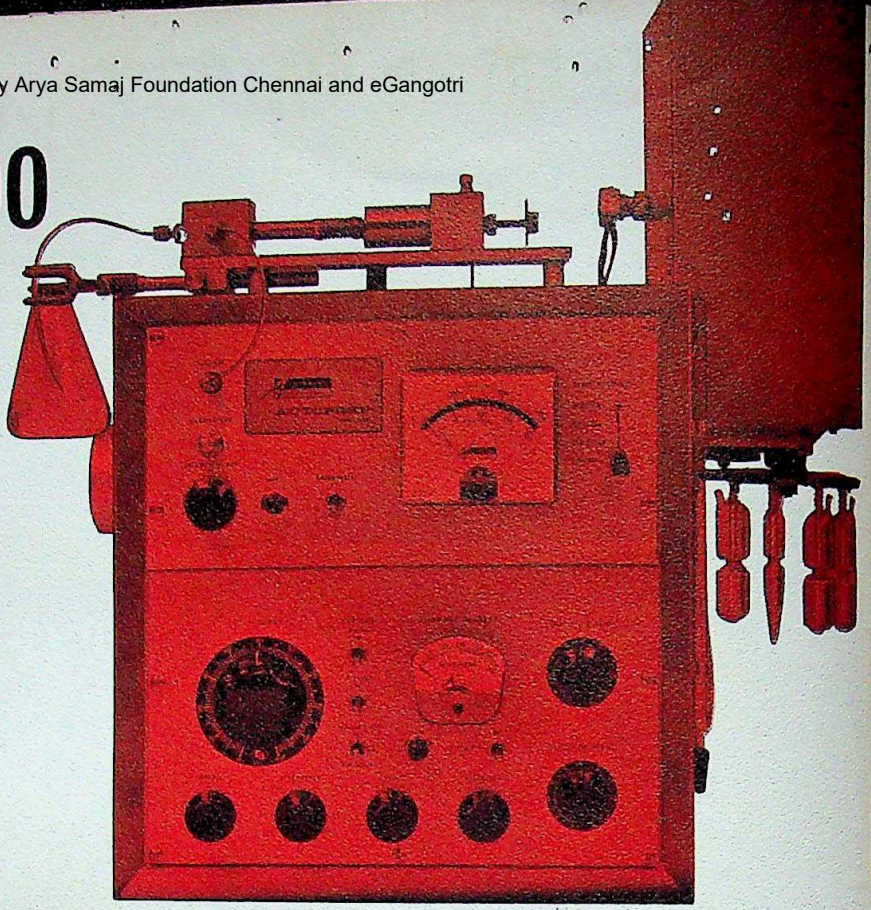
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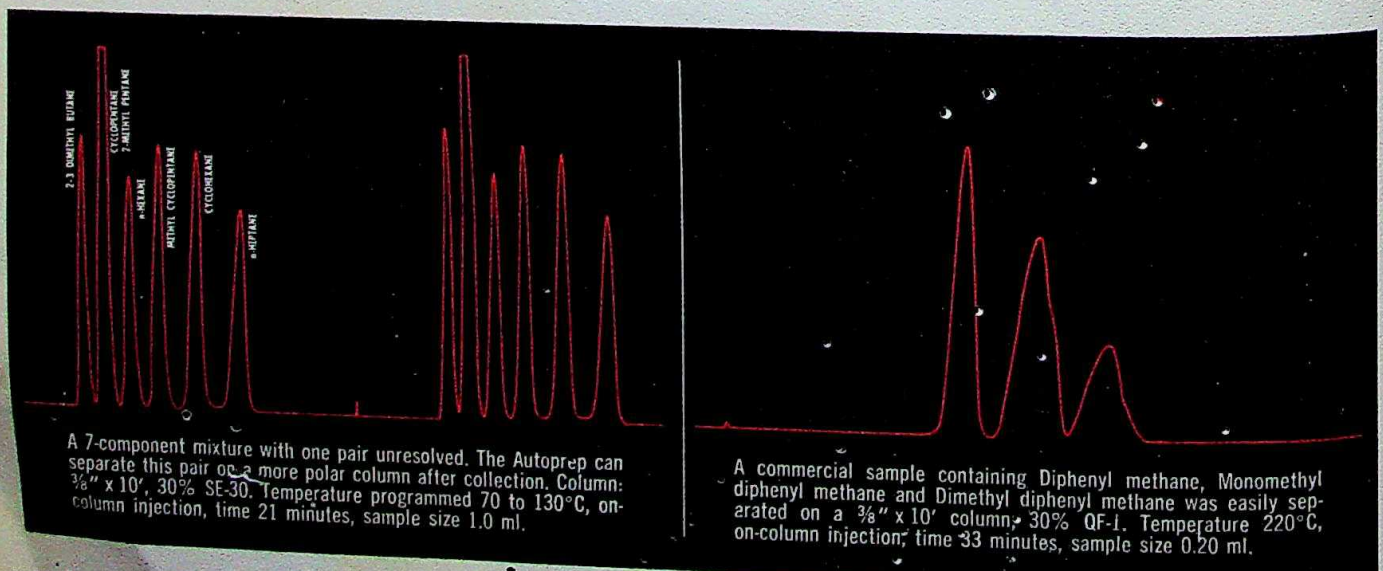
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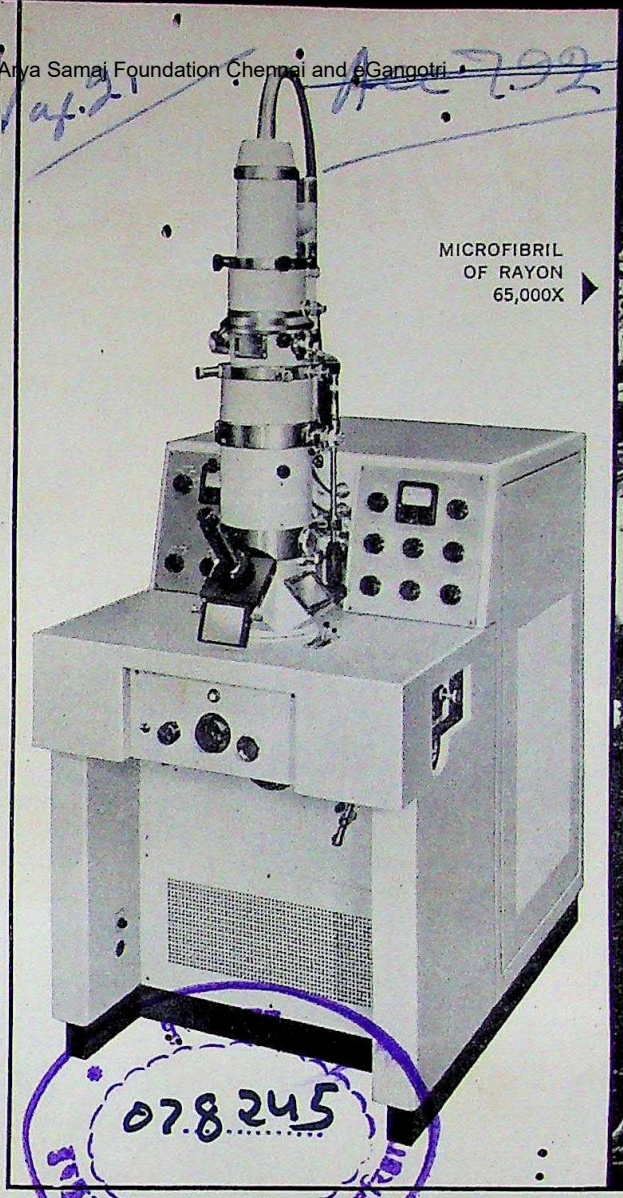
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Acknowledgment

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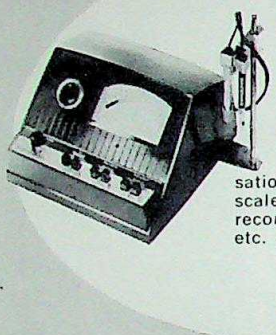
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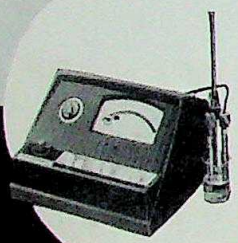
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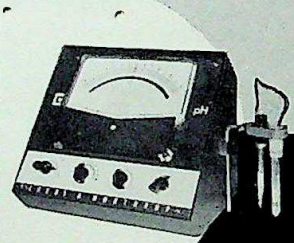
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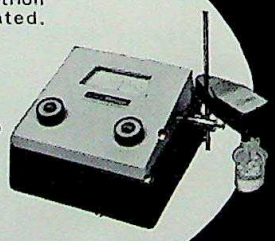
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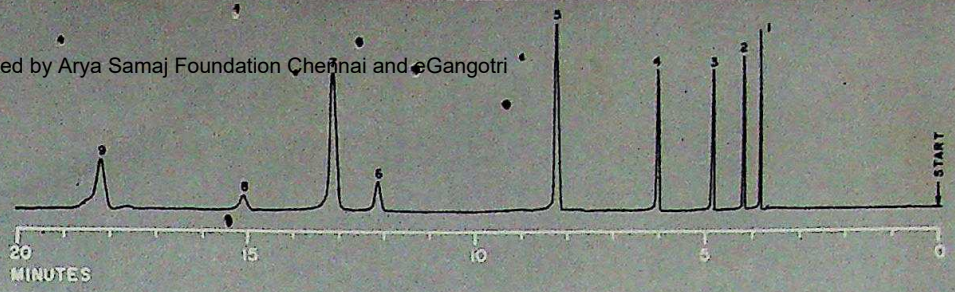
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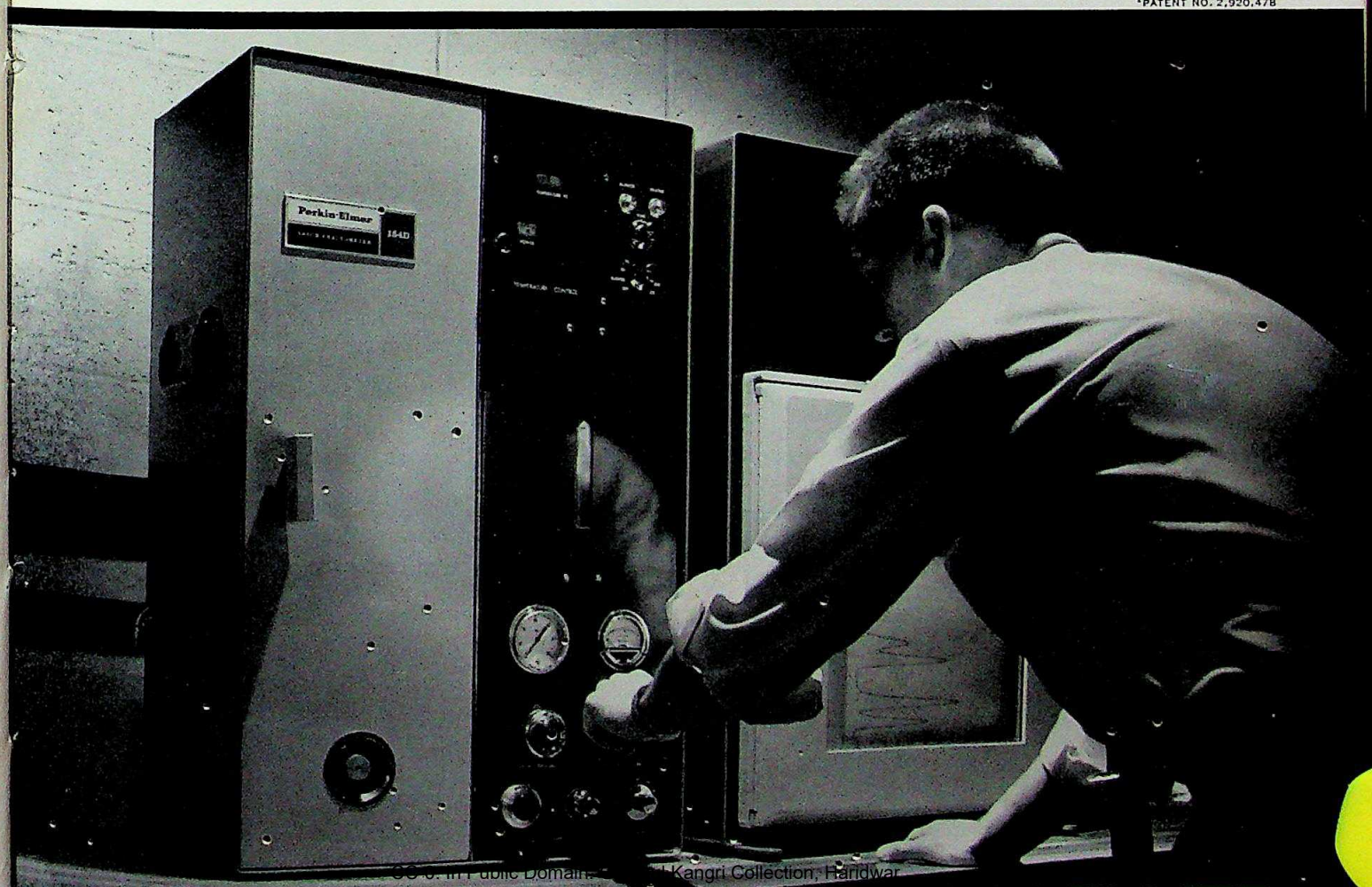
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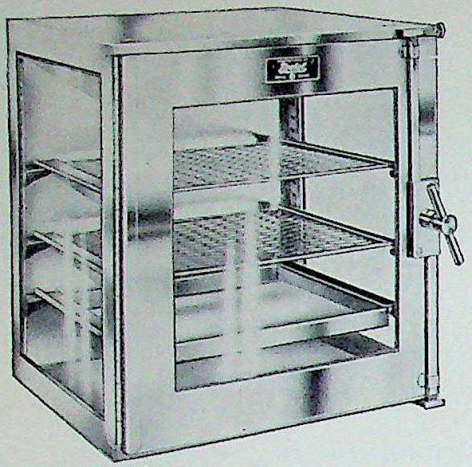
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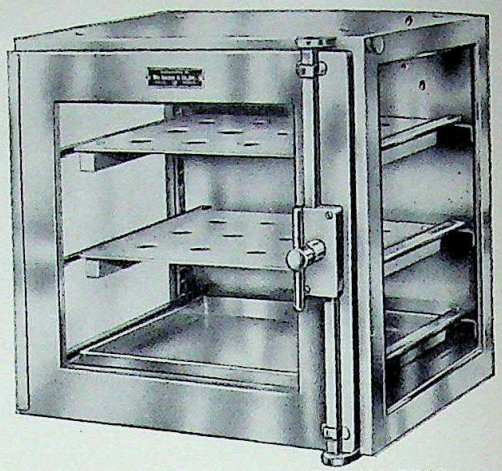
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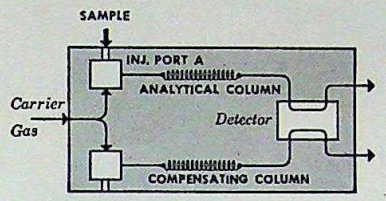
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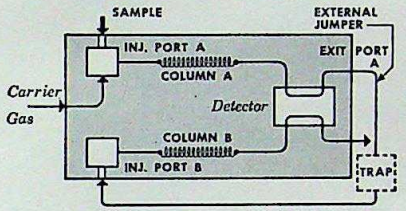
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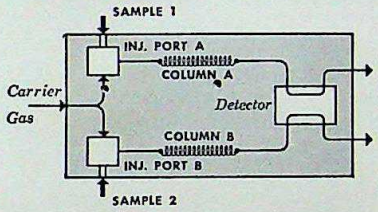
unique two-column design. The F & M designers equipped the Model 720 to provide five different column arrangements, each of which performs a valid function in the field of gas chromatography analysis.



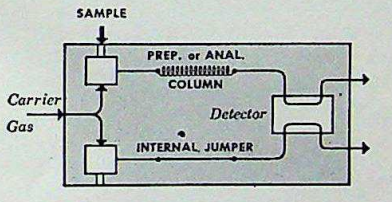
1 **Dual Compensating Columns**—In this flow configuration, the Model 720 eliminates the effects of substrate bleeding and extends by as much as 100°C the upper limit to which a column can be programmed without baseline drift.



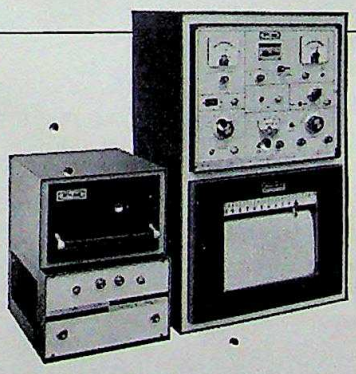
2 **Two Columns in Series**—In series operation, the 720 performs single-run analyses of difficult separations that require twice as much time on almost any other chromatograph. The analyst readily accomplishes series flow by connecting an external jumper between exit port A and injection port B.



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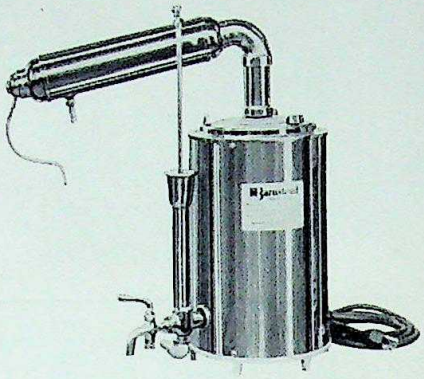
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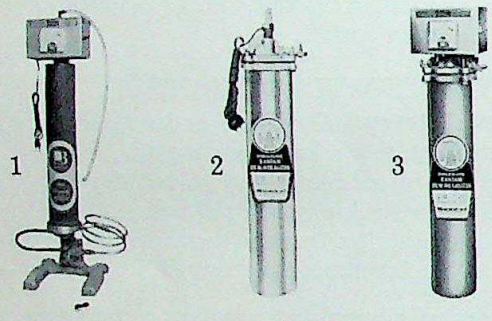
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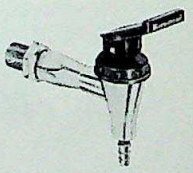


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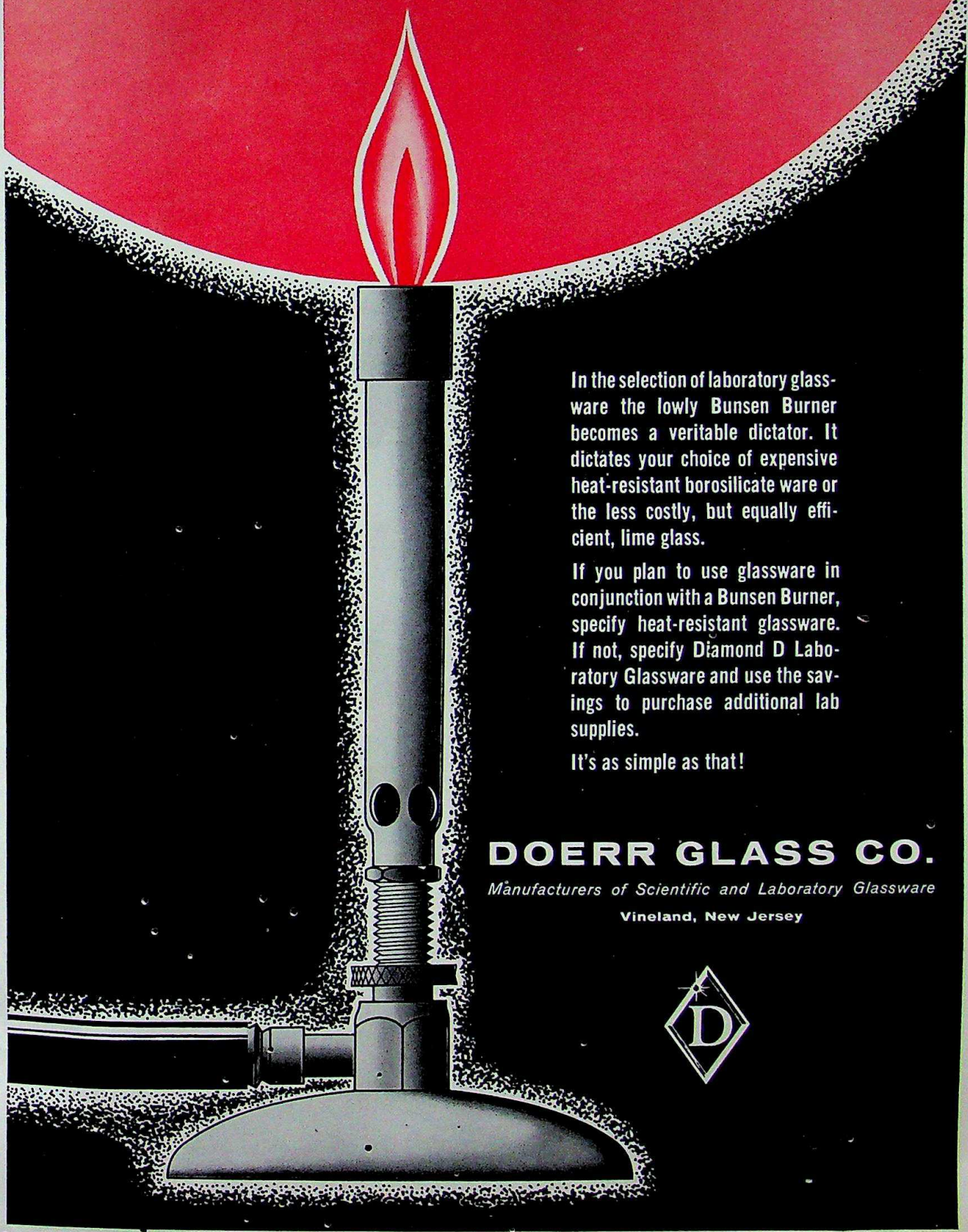
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2. OXYGEN

C. Reactions With Oxygen Gas

Dem. 47—Cigarette + Oxygen

To show: The burning of a cigarette soaked in liquid oxygen.

Materials: Liquid air, a cigarette, tongs, alcohol burner, a 50 ml beaker, Grand Canyon cell H-4.

Procedure: (*a*) Half-cover the cigarette with liquid air in the beaker. Place on the stage and project. (*b*) After half of the liquid has boiled away, remove from the projector. Project the Grand Canyon cell H-4. Place an alcohol burner on the Grand Canyon, project it; light the burner. Now pick up the cigarette in the tongs, and bring that end which was immersed in the liquid to the alcohol burner flame.

Observation: The cigarette burns down fiercely to the mid-point.

Explanation: The nitrogen evaporates first; that portion of the cigarette which was immersed in the liquid air becomes oxygen-soaked, and burns rapidly. The remainder of the cigarette burns at its normal rate.

D. Some Oxidations

1. OXYGEN-RICH COMPOUNDS

Dem. 48—Na_2O_2 + I_2

To show: Oxidation using peroxides.

Materials: fresh sodium peroxide, iodine, a coke-bottle cap, dropper bottle of water, $^1/_4$ teaspoon measure, Grand Canyon cell H-4 protected by two extra $5 \times 5 \times {}^1/_8$ in. squares of glass.

Procedure: CARE. DANGER OF EXPLOSION. Use only quantities stipulated. Gently mix $^1/_4$ teaspoonful (no more) of Na_2O_2 with $^1/_4$ teaspoonful (no more) iodine flakes. Place in a coke-bottle cap on cell H-4 and project. Keeping hand well away, drop a single drop of water on one side of the mixture.

Observation: Violent reaction, violet fumes of iodine are liberated from the heat of reaction.

Dem. 49—Na_2O_2 + Sulfur

To show: Sulfur ignited by moist sodium peroxide.

Materials: Fresh Na_2O_2, coke-bottle cap, flowers of sulfur, dropper bottle of water, Grand Canyon cell H-4 protected with two extra $5 \times 5 \times {}^1/_8$-in. pieces of glass, $^1/_4$-teaspoonful measure.

Procedure: CARE; MIX ONLY AMOUNTS STIPULATED. Mix $^1/_8$ teaspoonful of Na_2O_2 with an equal volume of flowers of sulfur in a bottle cap. Project on the Grand Canyon. Cautiously add a drop of water.

Observation: Catches fire.

Reference: ZSOLDOS, F., AND BRAKO, F., *J. Chem. Educ.*, **20**, 305 (1943).

Dem. 50—Na_2O_2 + Paper + Ice

To show: Paper ignited by moistened sodium peroxide.

Materials: Fresh Na_2O_2, 2×2-in. square of tissue paper, $^1/_2$-in. cube of ice, coke-bottle cap, Grand Canyon cell H-4 protected with two extra $5 \times 5 \times {}^1/_8$-in. pieces of glass, $^1/_4$-teaspoonful measure.

Procedure: CARE; MIX ONLY AMOUNTS STIPULATED. Fold the paper twice to give a $^1/_2$-in. square, and place on the coke-bottle cap on H-4. Add $^1/_{16}$-teaspoonful (no more) of fresh Na_2O_2 powder on top of the paper. Place on H-4 and project. Now place the piece of ice on top of the cap, and focus it.

Observation: In about 15 sec the ice has melted sufficient water to react with the peroxide, igniting the paper.

Note: A ship, the *Black Falcon*, in Boston Harbor caught fire when cans of Na_2O_2, carried as an emergency supply of oxygen, burst open and spilled their contents on wet grease.

Reference: BILLINGER, R. D., *J. Chem. Educ.*, **3**, 897 (1926).

Dem 51—Na_2O_2 + Excelsior

To show: Wood ignited by moistened peroxide.

Materials: A $^1/_2$-in. ball of excelsior, fresh Na_2O_2, a $1^1/_2$-in. square of asbestos, Grand Canyon cell H-4 protected by two extra $5 \times 5 \times {}^1/_8$-in. pieces of glass.

Procedure: Place the ball of excelsior on the asbestos square on H-4, and sprinkle on it $^1/_8$-(no more) teaspoonful of fresh Na_2O_2. Project. Now add a single drop of water to one side of the ball.

Observation: In a few seconds the ball of excelsior ignites.

Reference: FORD, L. F., *J. Chem. Educ.*, **18**, 64 (1941).

Dem. 52—$KMnO_4$ + Glycerine

To show: Spontaneous ignition of potassium permanganate plus glycerine.

Materials: Finely ground $KMnO_4$, glycerine in a dropper bottle, plastic cap about $^1/_2$ in. in diameter, a $^1/_4$-teaspoon measure, Grand Canyon cell H-4 protected with two extra $5 \times 5 \times {}^1/_8$-in. sheets of glass.

Procedure: CARE: USE QUANTITIES STIPULATED. Place $^1/_4$-teaspoonful of $KMnO_4$ in the cap, making a depression in the center. Place on H-4 and project. Now add a single drop of glycerine.

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Observation: In less than a minute the mixture smokes, then ignites.

Dem. 53 —NH_4NO_3 + Zn + Iodine

To show: Spontaneous ignition of zinc with ammonium nitrate.

Materials: NH_4NO_3, zinc dust, iodine flakes, coke-bottle cap, dropper bottle of water, a $^1/_4$-teaspoon measure, Grand Canyon cell H-4 protected with two extra 5 × 5 × $^1/_8$-in. sheets of glass.

Procedure: CARE: USE QUANTITIES STIPULATED. Place $^1/_4$-teaspoonful of NH_4NO_3 in the cap, and cover with $^1/_8$-teaspoonful of zinc dust; on top of this place $^1/_8$-teaspoonful of iodine. Place on cell H-4 and project. Now add a single drop of water to one side of the pile.

Observation: In a few seconds clouds of white ZnO are produced, and sufficient heat is generated to give violet iodine vapors.

Dem. 54—Nitric Acid + Turpentine

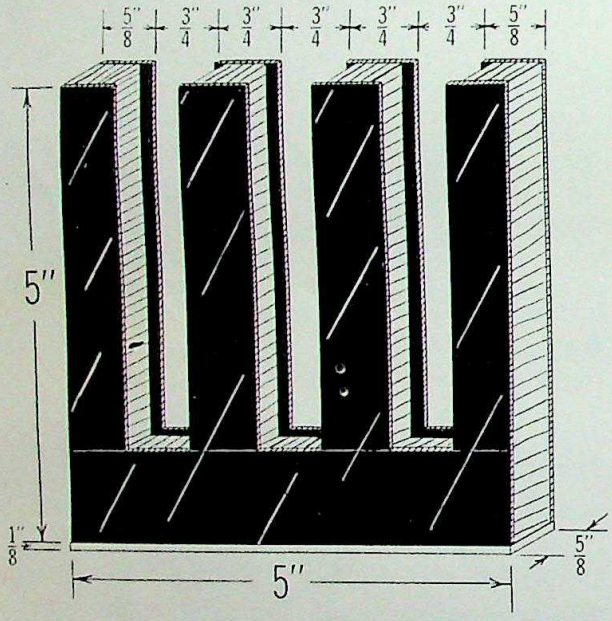
To show: Spontaneous ignition of turpentine dropped into a mixture of conc. H_2SO_4 + fuming HNO_3.

Materials: Fuming nitric acid, conc. H_2SO_4, turpentine, a polyethylene bottle cap about $^1/_2$ in. in diameter, Grand Canyon cell H-4 protected by two extra 5 × 5 × $^1/_8$-in. pieces of glass.

Procedure: Mix two parts of fuming nitric acid with one part conc. sulfuric acid in the plastic cap placed on H-4 and projected. CAUTIOUSLY add a single drop (no more) of turpentine to the acid mixture.

Observations: Violent sputtering; the mixture may ignite the turpentine and evolve clouds of black smoke (carbon).

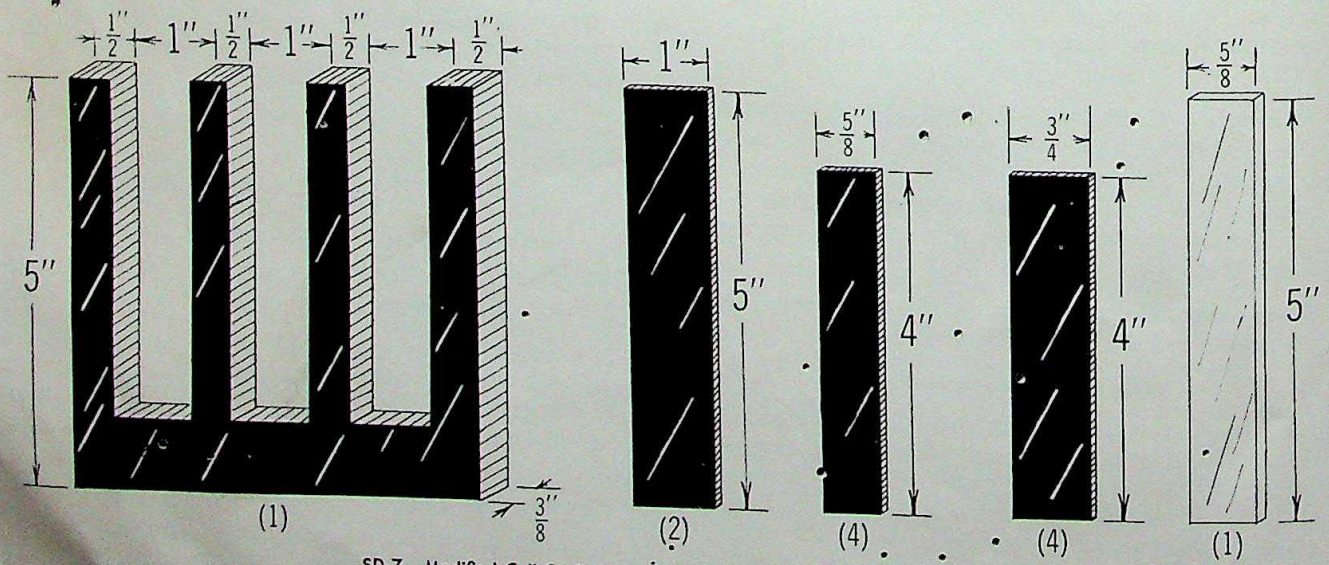
SUPPLEMENTARY DEVICES



SD-7 CELL C-g2 (glass, model 2)

For experiments carried out in glass culture tubes the new model C-g2 described here is superior to Cell C-g described in the first issue of this series. Cell C-g2 is an open skeleton of plastic into which the culture tubes slip. Diagram SD-7 below, showing the parts of the device is self-explanatory. In assembling C-g2 moisten the parts with cement, place them together, insert culture tubes in the slots, and hold the tubes in place while the cement is hardening. In this way one can can achieve proper alignment of the slots. Henceforth in this series C-g will be discarded and C-g2 used instead, so it would be well for the reader to mark his copy in the *J. Chem. Educ.*, **39**, 14 (1961) to this effect.

(*To be continued in February*)



SD-7 Modified Cell C-g2 above (with parts of C-g2 shown below)

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Out of the EDITOR'S BASKET

Edited by William G. Kessel

When writing for additional information about new products or for new literature, your inquiry will receive prompt attention if you write on your firm or institution letterhead and mention the Journal of Chemical Education and the date of the particular issue. Pamphlets, booklets and similar literature are gratis unless otherwise specified.

New Apparatus and Equipment

▶ A new line of high-pressure Glasteel reactors ranging in size from one to five gallons capacity is now available for laboratory applications from The Pfaudler Co., a division of Pfaudler Permutit Inc., Rochester, New York.

▶ A new series of temperature chamber safety controls, designed to protect test specimens, is being manufactured by Associated Testing Laboratories, Inc., Route 46, Wayne, New Jersey.

Three models in the TL series, TL-A, TL-B and TL-C, are adaptable to any make and model of low or high temperature chamber. They can be used with either cascade refrigeration, CO_2 refrigeration type chambers or high temperature ovens.

▶ Tracerlab, a division of Laboratory for Electronics, 1601 Trapelo Rd., Waltham 54, Massachusetts, has developed a new low temperature ashing system which provides unique method of oxidizing organic samples. It permits complete ashing at rates up to 1 gram per hour and at temperatures below 100°C.

▶ An all-polyethylene syphon with a built-in "self-starter" is now available from General Scientific Equipment Co., 7516 Lime Kiln Pike, Philadelphia 50, Pennsylvania.

▶ A new Norelco EM-75C electron microscope, highly recommended as a tool for teaching and general service applications because it is easy to operate and maintain and has low down-time, has been announced by Philips Electronic Instruments, 750 S. Fulton Ave., Mount Vernon, New York.

▶ The Bristol Co., Waterbury 20, Connecticut, announces development of a new wide chart potentiometer with a pen speed of less than 0.2 sec. The time interval applies to full scale travel across a 10-in. calibrated width. The company also offers an electric selectomatic recorder, a multipoint instrument enabling the operator to delete unchanging variables from the printing program and permitting more frequent printing of desired variables.

▶ Andrew Technical Supply Co., 1824 W. Kinzie, Chicago 22, Illinois, announces a new series of motor-driven Tumble jars, equipped with gear reduction drive and explosion proof motors.

▶ A newly designed, high-vacuum, high-capacity industrial pump that smoothly handles corrosive gases or high viscosity materials has been developed by the Nelson Vacuum Pump Co., 2133 Fourth St., Berkeley 10, California.

▶ California Laboratory Equipment Company, 1717 Fifth St., Berkeley 10, California, offers a high vacuum, low temperature Model C rotary evaporator which eliminates all reactive metal, rubber or grease surfaces and seals to assure consistently uncontaminated yields.

▶ Yellow Springs Instrument Co., Box 106, Yellow Springs, Ohio, announces the availability of a unique new form of its precise thermistor family. The precise thermistors are mounted in 2-in. Teflon probes which can be formed to any configuration required by the user with just finger pressure.

▶ Micro-Tek Instruments, Inc., 550 Oak Villa Blvd., Baton Rouge, Louisiana, announces the GC 1600 Series of temperature programmed gas chromatographs.

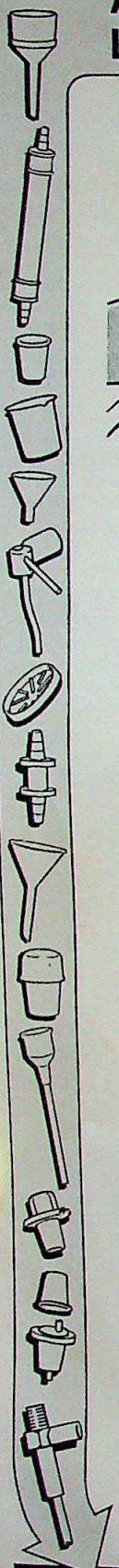
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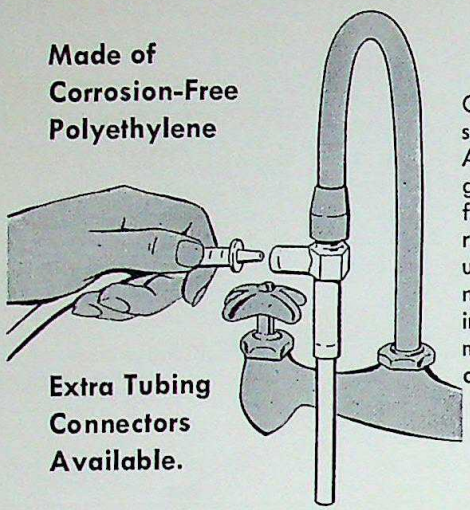


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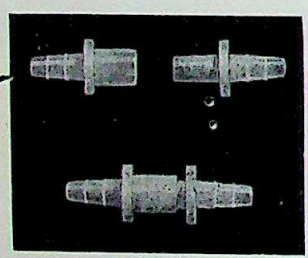
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These instruments are all equipped with ionization detectors, with a choice of hydrogen flame, argon triode, or electron capture and micro universal inlet system and variable inlet splitter as standard equipment.

▶ A new low cost ion vacuum system, the Eduvac, which electronically produces ultra-high (5×10^{-8} mm of mercury) ultra-clean vacuums has been introduced by Atomic Laboratories, Inc., 3086 Claremont Ave., Berkeley 5, California.

▶ A new series of custom engineered miniature, self-contained compressor-dehydrators, designed to supply clean, dry, oil-free air for small capacity equipment, has just been made available by Trinity Equipment Corp., Cortland, New York.

▶ A residual gas analyzer capable of detecting minute quantities of gas remaining in evacuated systems has been introduced by Consolidated Electrodynamics Corp., 360 Sierra Madre Villa, Pasadena, California. Essentially a mass spectrometer without a vacuum system, the new Type 21-613 RGA is capable of detecting gases with partial pressures as low as 5×10^{-11} mm Hg.

▶ Separation of large quantities of proteins and related compounds (up to 200 ml blood serum) is described as being normal for a new apparatus from LKB Instruments, Inc., 4840 Rugby Ave., Washington 14, D. C., called the Porath preparative electrophoresis column. Drs. J. Porath and B. von Hofsten of the Department of Biochemistry, Uppsala University, Sweden, have reported the separation of 125 ml of crude extract from 150 g of *E. Coli* from a single run of 47 hours, including elution.

▶ The newly developed Micro ATR Unit makes it possible to accomplish direct infrared analysis of minute samples—such as chemical residue, strands of fiber, and even tiny fragments of tissue as small as 1 mm wide by 4 mm long without special sample preparation. Write Connecticut Instrument Co., 30 Commerce Rd., Stamford, Connecticut.

▶ Sharp Laboratories, Inc., P.O. Box 2078, LaJolla, California, offers a fine inch diameter detector for alpha and beta counting systems and the CDL-14, a complete laboratory for carbon dating (for samples to 45,000 years old).

▶ Waters Associates, Inc., 45 Franklin St., Framingham, Massachusetts, in conjunction with Proctor and Gamble has developed a new miniature detector for monitoring the effluent of liquid chromatography columns. The development of liquid-liquid chromatography and liquid-solid chromatography has lagged far behind gas chromatography because of the lack of a universal, sensitive detecting device.

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Out of the EDITOR'S BASKET

▶ Thermolyne Corp., 471 Huff St., Dubuque, Iowa, announces a few macro dri-bath, Type 6900 designed to accommodate test tubes up to 20 mm od at 100°C ± ½°C and Type 6700 for use at 37°C or 56°C, as desired.

▶ Electronic Instruments for Research, Inc., 4135 Hayward Ave., Baltimore 15, Maryland, has made available a column conditioner that is compatible with their Model AU-8 gas chromatograph. However, the conditioner is capable of conditioning columns for any gas chromatograph up to sixteen feet.

New Literature

● An attractive brochure on a new line of instruments for chemical analysis has just been published by Golden Instruments, Inc. Featured are several models of the Golden spectrophotometer and recording spectrophotometer at exceptionally modest prices. Copies of the brochure may be had by writing direct to Golden Instruments, Inc., 2519 N. Elston Ave., Chicago 47, Illinois.

● Reports of experimental work on a new type ion retardation resin, AEllA8 and new material and bibliography of the literature are available from Bio-Rad Laboratories, 32nd & Griffin Ave., Richmond, California.

● Mettler Instrument Corp., 20 Nassau St., Princeton, New Jersey, is offering literature on a 650 pound marble table designed for use with analytical balances.

● Sulfrian Cryogenics, Inc. has announced an across-the-board price reduction on its line of standard containers for the transport, storage and handling of liquefied gases. For the *new* price list and detailed information, contact Sulfrian Cryogenics, Inc., 1290 Central Ave., Hillside, New Jersey.

● *Tables of Einstein Functions; Vibrational Contributions to the Thermodynamic Functions*, by Joseph Hilsenrath and Guy G. Ziegler, National Bureau of Standards Monograph 49, issued July 12, 1962, 258 pages, $2.75. (Order from the Superintendent of Documents, U. S. Government Printing Office, Washington 25, D. C.)

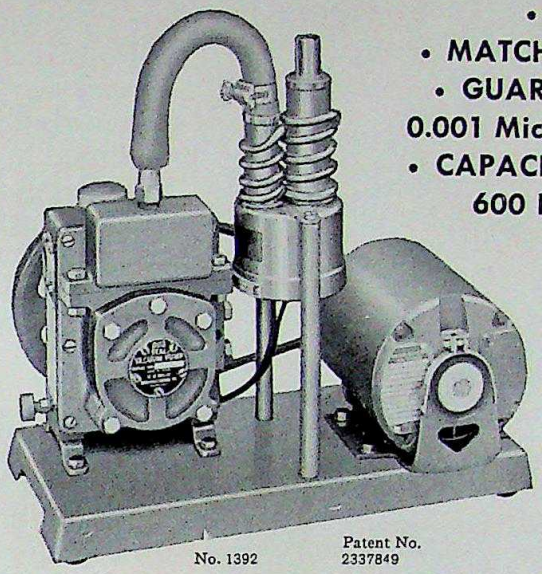
This monograph is one of a series of National Bureau of Standards publications presenting definitive thermodynamic data of interest in pure and applied science and in technology. The tables of Einstein functions should be useful in estimating the thermodynamic properties of polyatomic gases at high and low temperature, as well as the heat con-

(*Continued on page A35*)

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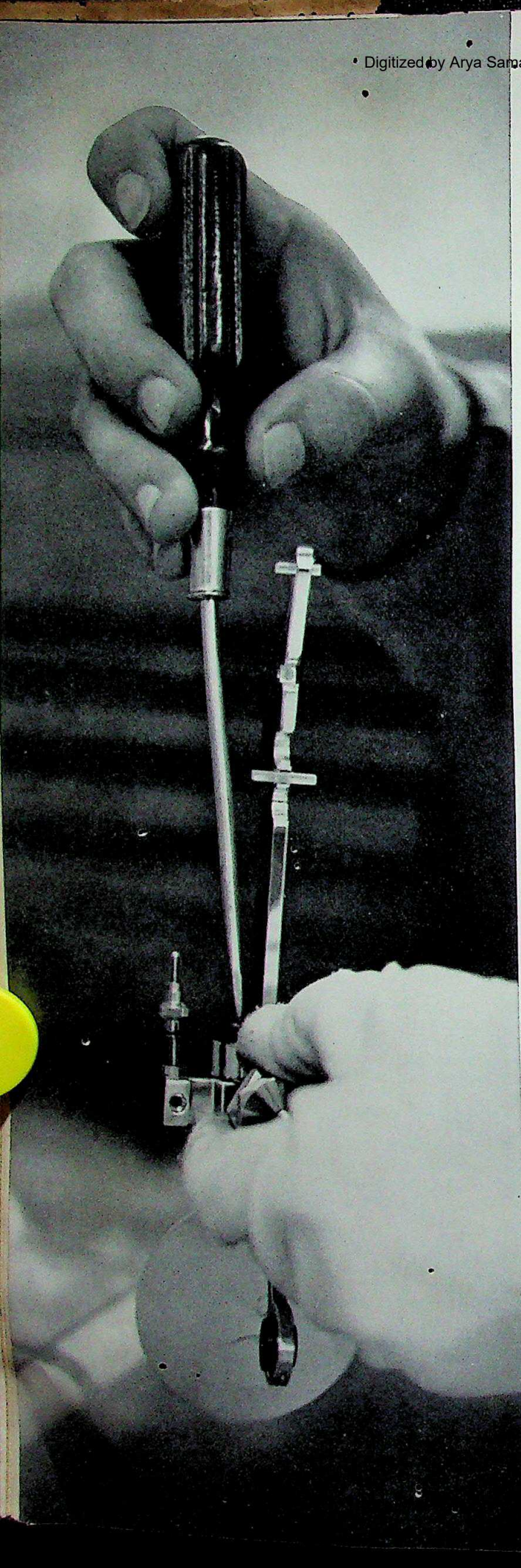
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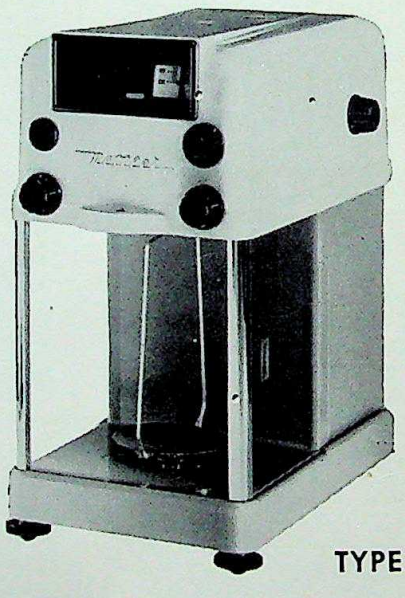


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● Mixing Equipment Co., Inc. 170 Mt. Read Blvd., P. O. Box 1370, Rochester 3, New York has published a new 20-page brochure, *B-540*, on the profitable selection and use of portable mixers in the 1/4 to 3 hp range.

● Details on the "Vacutherm," a micro furnace for use with inverted metallurgical microscopes, designed specifically for the observation of thermal transition phenomena in metals and alloys is available from William J. Hacker & Co., Inc., P.O. Box 646, West Caldwell, New Jersey.

● *Technical Bulletin No. 1001* gives information on the new crystals developed for laser work by Isomet Corp., 433 Commercial Ave., Palisades Park, New Jersey.

● The Stackpack, a bench-scale, turn-key plant for laboratory evaluations of electrodialysis, is now available from Ionics, Inc., 152 Sixth St., Cambridge 42, Massachusetts. Ask for *Bulletin L-2*.

● Olin Mathieson Chemical Corp., Organics Division, 400 Park Ave., New York 22, N. Y., has prepared a brochure describing its new glycerine plant, the method of production, and details on some of the many uses and handling of the material.

● *European Chemical News*, a weekly giving speedy, accurate information on the chemical industry in Britain and other countries with emphasis on Europe is available from Temple Press Limited, Bowling Green Lane, London, ECI, England. Regular delivery for one year $7.50, air mail $26.70.

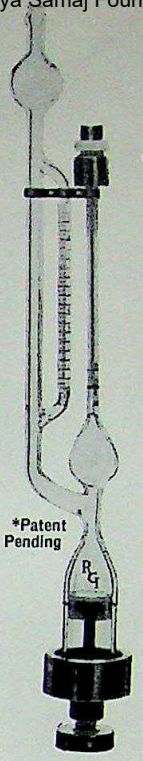
● A brochure describing new types of industrial gamma gauging systems and their applications is now available from Nuclear Research Corp. of Southampton, Pennsylvania.

● New data sheets on pure rhodium and pure iridium crucibles and on trilay noble metal, laboratory ware are now available through the Technical Service Department, Baker Platinum Division of Engelhard Industries, Inc., 113 Astor St., Newark 14, New Jersey.

● Texas—U. S. Chemical Co., P.O. Box 98 Parsippany, New Jersey, offer two bulletins with up-to-date information on butadiene as a raw material, titled *Butadiene Sulfone* and *Butadiene for Tetrahydrobenzaldehyde*.

● A 16-page illustrated brochure covering economical electronic controls for industry has been published by the Apparatus Controls Division of Minneapolis-Honeywell, Minneapolis 8, Minnesota. The

(*Continued on page A36*)



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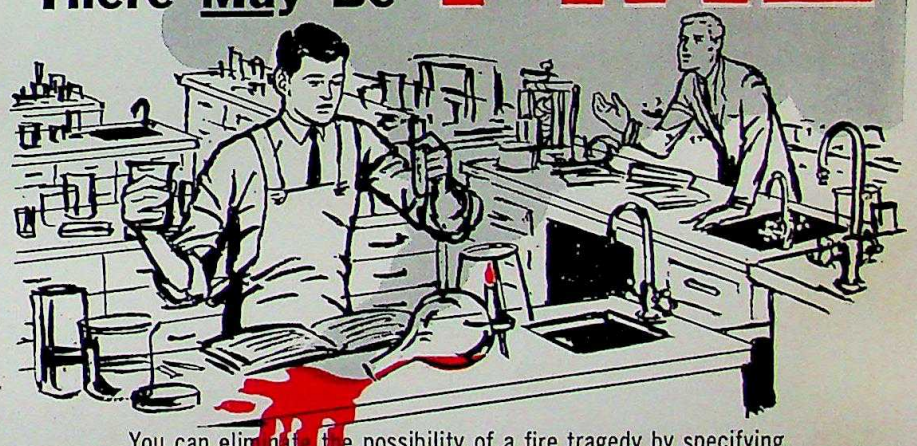
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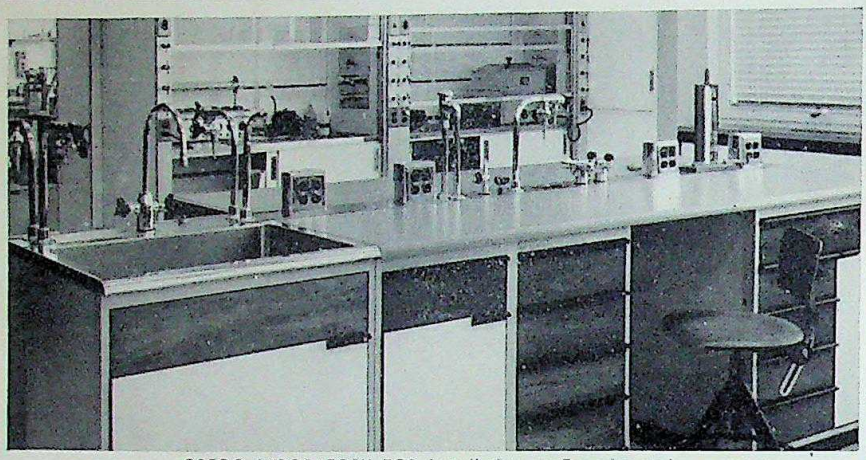
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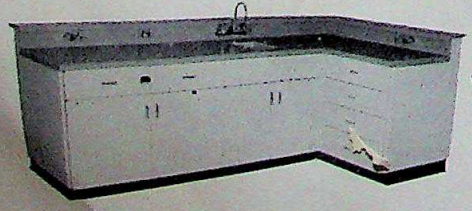


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- GREGG TOPS do not have an applied or polished surface which loses resistance value when scratched or worn.



For more information write for brochure #655 and test reports

GREGG LABORATORY TOPS.
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Out of the EDITOR'S BASKET

booklet discusses controls for temperature, humidity, liquid levels, motor positions and ice-making machines, and lists prices.

● A collection of 500 case histories of accidents in the chemical industry has been compiled into book form by the Manufacturing Chemists' Association, 1825 Connecticut Ave., N. W., Washington 9, D. C. *Case Histories of Accidents in the Chemical Industry* is $2.50 a copy. "Behind this unique joint endeavor," the Association states in a foreword to the book, "is the compelling concern of chemical industry management for the welfare of industry employees. It reflects an open resolve by members of the industry that any mistakes or omissions of today will not be repeated tomorrow."

● Cenco Instruments Corp., 6450 W. Cortland St., Chicago 35, Illinois, have initiated a new publication *Cenco International News* designed to keep customers and friends in the free world, informed.

● Publication of the second edition of American Petroleum Institute *Toxicological Reviews on Cyclohexane and Styrene* was announced recently. These new reviews and previously-announced second editions on copper naphthenate, naphthalene, naphthenic acids, butadiene, benzene, toluene, and xylene may be obtained from the Publications Section, American Petroleum Institute, 1271 Avenue of the Americas, New York 20, N. Y. The price is 25 cents a copy.

● Electronic Instruments for Research, Inc., 4135 Hayward Ave., Baltimore, Maryland, has free literature available on their gas chromatographs, dual temperature column conditioners, liquid scintillation counting systems for radioactive measurement of effluent components, and electrometer and high voltage supply.

● A four page bulletin describing the Model 770 automatic preparative gas chromatograph has been published by F & M Scientific Corp., Route 41 and Starr Rd., Avondale, Pennsylvania.

● Users of maleic anhydride will be interested in a technical publication of the Plastics Division, Allied Chemical Corp., titled *Safe Handling of Maleic Anhydride*. Copies may be obtained from the Plastics Division, Allied Chemical Corp., 40 Rector St., New York, N. Y.

● The new Cenco Hyvac*28, a high-speed high vacuum pump, and an extensive line of other vacuum components are fully described in a new four-page, two-color brochure recently published by Central Scientific Co., 1700 W. Irving Park Rd., Chicago 13, Illinois.

● A bulletin of the new electron spin resonance spectrometer system AL 340SY

(*Continued on page A40*)

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these "new look" OHAUS spring scales are at the head of their class . . . . .

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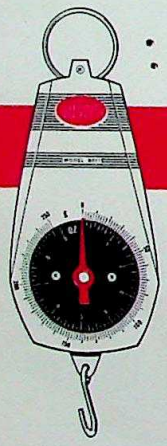


SPRING SCALES . . . (Pull Type)

For general experimental work when greater convenience and accuracy of dial scale are not required. Three ranges available all with graduations in both metric and avoirdupois.

List Price $2.50

MODEL NUMBER	GRADUATIONS	ACCURACY AT FULL LOAD	LIST PRICE
8001	250 g x 10 g 9 oz. x ¼ oz.	± ⅛ oz. (½ avd. grad.)	
8002 (P.G. No. 0230)	500 g x 20 g 18 oz. x ½ oz.	± ¼ oz. (½ avd. grad.)	$2.50
8004	2000 g x 25 g 72 oz. x 1 oz.	± 1 oz. (1 avd. grad.) or ± 25 g (1 metric grad.)	

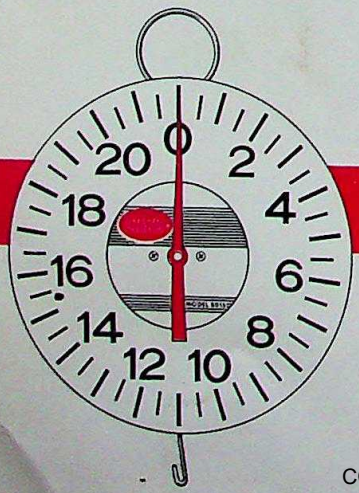


DIAL SPRING SCALES

This type scale provides greater accuracy because vertical spring movements are magnified through rack and pinion with readings made on a large circular dial. Three ranges available in combination metric and avoirdupois.

List Price $2.75

MODEL NUMBER	GRADUATIONS	ACCURACY AT FULL LOAD	LIST PRICE
8011	250 g x 2 g 9 oz. x ⅛ oz.	± 2 g (1 metric grad.)	
8012 (P.G. No. 0240)	500 g x 5 g 18 oz. x ¼ oz.	± 5 g (1 metric grad.)	$2.75
8014	2000g x 10 g 72 oz. x ½ oz.	± 20 g (2 metric grad.)	



DEMONSTRATION SPRING SCALE

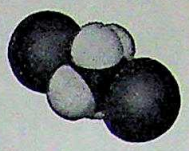
Ideal for use in demonstration work where it is desirable for many people to be able to read the scale at the same time. Frosted aluminum dial plate 8¼" diameter has ¾" black numerals. Graduations are 20 units by ½ unit with each unit equal to 100 grams. Intermediate graduations are shorter and narrower for easy reading.

Model 8015—List Price $6.50
(P.G. No. 0245)

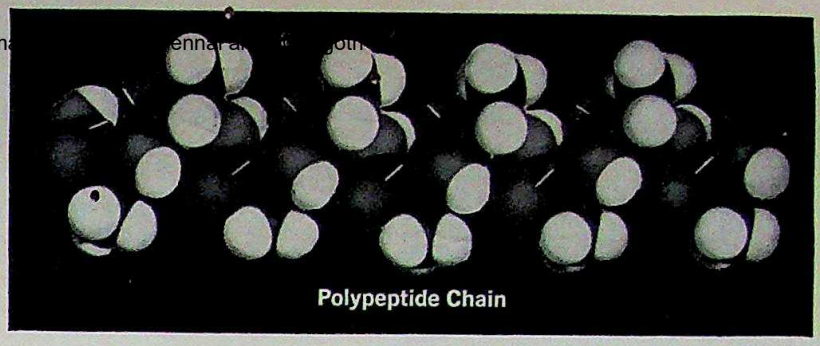
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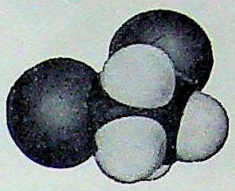
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Trans-
Dichloroethane

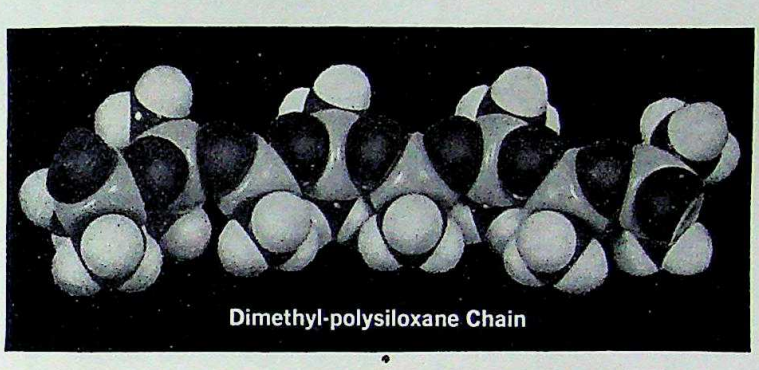


Cis- ("angular")
Dichloroethane





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LaPine-Leybold models are invaluable aids in studying three dimensional arrangements of macromolecules, various types of steric effects, biochemical specificity, geometrical and optical isomerism, tautomerism, resonance and other chemical phenomena.

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No. CE302-81 Supplementary Set of 40 pieces of 13 Different Types, each . . . . . $ 58.30

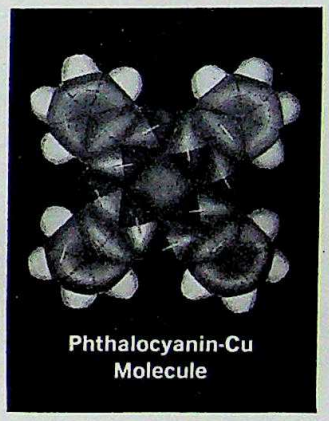
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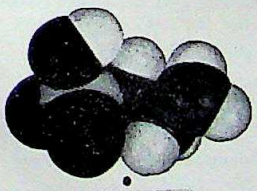
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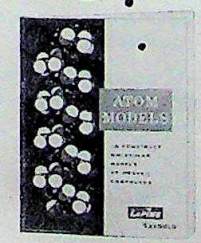
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Phosphoric Acid





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2. Booklet on Atom Models for Schools, with details of 9 models and information on constructing many compounds, 16 pages, 3 colors.
3. Price List on 47 models available as individual pieces.

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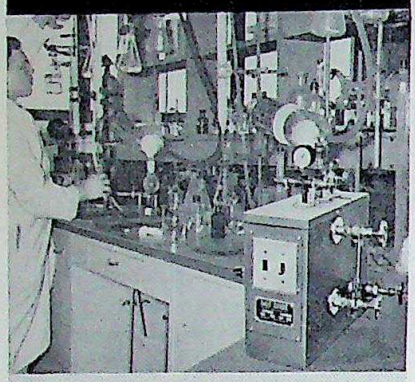
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Out of the EDITOR'S BASKET

which is designed for basic research studies in the fields of solid state physics, organic and physical chemistry, and biology is available from Alpha Scientific Laboratories, P.O. Box 333, Berkeley 1, California.

● A new 16-page *Bulletin 19-12C, Simplified Instrumentation for pH Measurement and Control,* describes the full line of pH instruments and accessories offered by The Foxboro Co., Foxboro, Massachusetts.

New Chemicals

◇ A new price list titled *New Volk Tritium and Carbon-14 Compounds* just issued by Volk Radiochemical Co., Skokie, Illinois, briefs the chemical specifications, packaging, specific activity, and pricing schedules for twenty-five new radioactive chemicals.

◇ Kits for glass fiber paper (GFP) chromatography are now available from Applied Science Laboratories, Inc., State College, Pennsylvania.

Miscellany

★ Narrated by John Charles Daly, a "Documentary in Sound" traces the development of the space age in America from the first rudimentary experiments in rocketry to the present Moon Shot program. Over seventy-five authentic sounds of the times are included, each recorded in high fidelity. "The Space Age/The Age of Reliability" lends historic perspective to the events that have shaped the space age—and to the impact of this new age on America—and American Industry. For a complimentary album, address Raybestos-Manhattan, Inc., Passaic, New Jersey, on your letterhead.

★ Two celluloid devices for assisting the chemistry student; "Stencil for the Reproduction of Structural Formulae and "Calculator for Electron Distributions in the Periodic System" are available from Verlag Chemie, GMBH, Weinheim/Bergstr, Germany. The stencil sells for $3.75 and the calculator $2.50.

★ Two new wall charts, oxidation-reduction half reactions and atomic orbital, for use in school and college level chemistry teaching and based upon recommendations made by the CHEM study group have been introduced by Central Scientific Co., 1700 W. Irving Park Rd., Chicago 13, Illinois. They feature extra large lettering for maximum classroom visibility.

(*Continued on page A42*)

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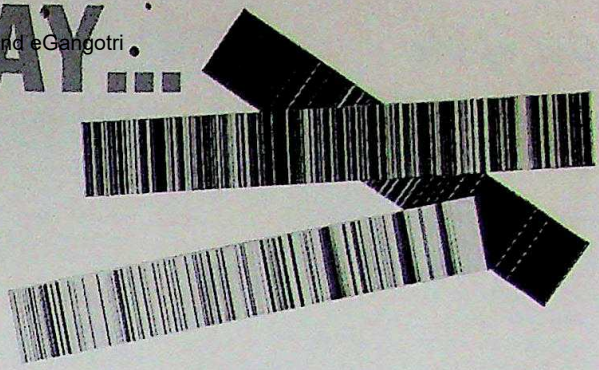
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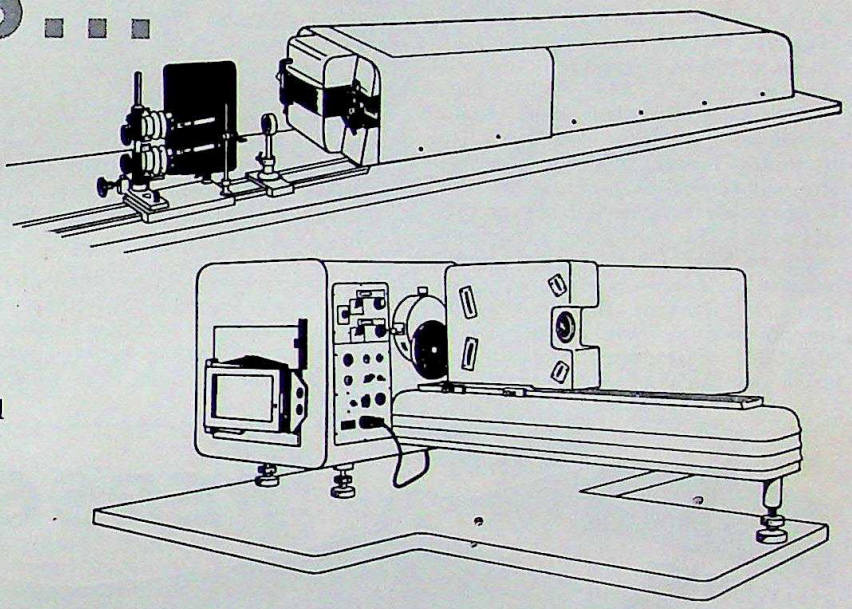
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Out of the EDITOR'S BASKET

★ For the past seven years the Comparative Education Society has sponsored comparative education seminars and field studies abroad. These have been intensive first-hand studies of educational institutions as they operate in the larger cultural milieu. Participation in the program is open to anyone interested in the international character of education. The Comparative Education Society and Phi Delta Kappa invite all interested persons to send their inquiries to Dr. Gerald H. Read, Secretary-Treasurer, Comparative Education Society, Kent State University, Kent, Ohio. An application for participation will be sent to you.

★ The October issue of the Monsanto Magazine features an answer to Rachel Carson's "Silent Springs," entitled "The Desolate Year." This article begins, "Does the world really need chemical pesticides? Are these compounds (used to control insects, rodents, weeds, parasites and plant diseases) better left alone? Is the public being sold a monstrous bill of goods? The answers to those questions could be learned with finality by seeing what would happen if pesticides were not available. Imagine, then that by some incomprehensible turn of circumstances, the United States were to go through a single year completely without pesticides." Then the article tells what would produce "The Desolate Year."

★ A new atom model, for cyclobutane, has been added to the list of LaPine-Leybold atom models for organic chemistry researchers and instructors being distributed by LaPine Scientific Co., 6001 S. Knox Ave., Chicago, Illinois. Like the others in the line, the new model is made by E. Leybolds Nachfolger, Cologne, W. Germany.

★ "Conversion of Heat Into Useful Work" is the subject of a new 16mm educational film released recently by Cenco Educational Films, 1700 W. Irving Park Rd., Chicago 13, Illinois.

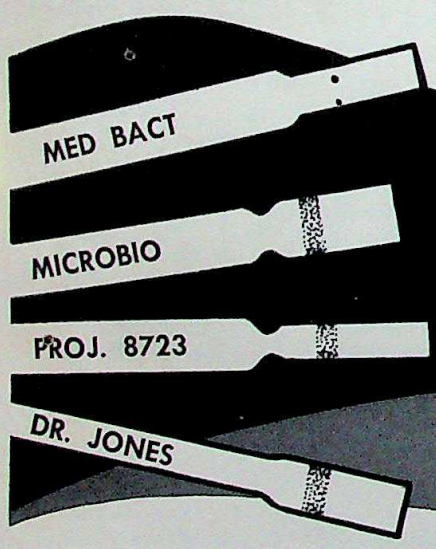
★ Graduate engineering study and fundamental research in plastics leading to the degree of Master of Science in Engineering; particularly suited to chemical, electrical and mechanical engineers, and to chemists and physicists. Outstanding graduates may become Ph.D. candidates in the departments of Mechanical or Chemical Engineering with support of the Plastics Program. For further information regarding curriculum, fellowships, research assistantships and application forms, address: Prof. Louis F. Rahm, Director, Plastics Laboratory, Princeton University, Princeton, New Jersey.

★ Four Awards of five hundred dollars each for the best scientific articles or theses on meat sciences, including biochemistry, nutrition, and animal breeding and husbandry will be made after competitive judging on the basis of educational and scientific contribution. Publication is expected for the benefits of scholars generally. For details contact: Mr. John A. Killick, Secretary-Treasurer, The Wilbur LaRoe, Jr., Memorial Foundation, 740 Eleventh St., N. W., Washington 1, D. C.

★ An International Research Symposium will highlight a week devoted to gas chromatography at the University of California, Los Angeles, January 28–February 1, 1963. Dr. Robert L. Pecsok, Professor of Chemistry, announces a program of distinguished chemists from abroad who will discuss "Recent Advances in Gas Chromatography," emphasizing their own work.

The fifth short course in "Fundamental Principles of Gas Chromatography" will be held January 30–February 1. This intensive three day course is presented in response to many requests from industry and is an up-dated version of the very successful previous courses.

The two programs are independent and both are jointly sponsored by the Department of Chemistry, Engineering Extension, and Physical Sciences Extension, with Dr. Pecsok as the Coordinator. Fee for the two day Symposium will be twenty-five dollars, and for the three day course one hundred dollars. Additional information and application blanks may be obtained by phoning or writing to H. L. Tallman, Physical Sciences Extension, Room 6532 Engineering Building, University of California, Los Angeles 24, California.



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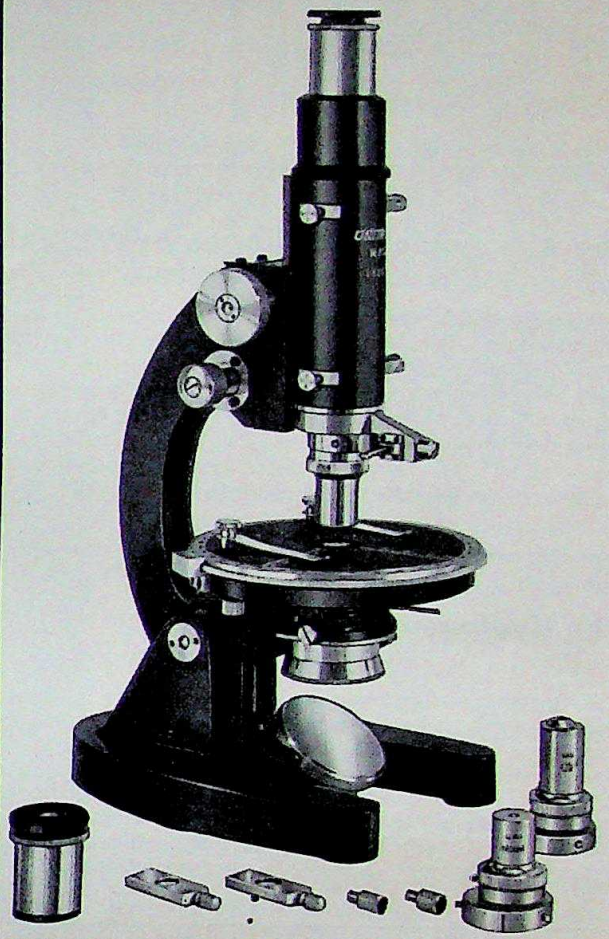
FIRST: LOOK AT UNITRON'S NEW POLARIZING MICROSCOPE

Here is a precision measuring instrument for both orthoscopic and conoscopic observations, designed to meet the exacting requirements of science, education, and industry. Its many features make it ideal for work in chemistry, crystallography, mineralogy and biology as well as in the technology of paper, glass, textiles and petroleum.

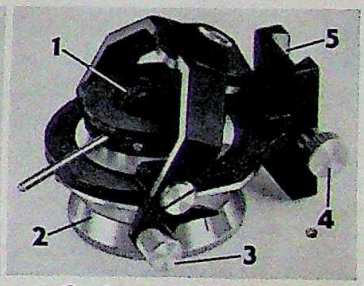
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Note that UNITRON'S new Model MPS comes complete with optics and accessories and includes features usually associated only with much more costly models.

- **EYEPIECES:** Micro 5X providing measurements to 0.0025mm. and cross-hair 10X. The eye lenses focus to produce sharp reticle images and are keyed to prevent rotation.
- **OBJECTIVES:** 4X(N.A.0.1), 10X(N.A.0.25), 40X(N.A.0.65), achromatic, strain-free, each with centerable mount.
- **NOSEPIECE:** quick-change type for critical centering.
- **CONDENSER and POLARIZER:** three-lens condenser with upper elements on a swing-out mounting, provides either parallel or convergent light. A dovetail-slide focusing mount and iris diaphragm insure optimum illumination and resolution.
- **POLAROID POLARIZER:** rotatable through 360° and graduated every 45°. Plano-concave mirror.
- **ANALYZER:** Polaroid, in sliding metal mount.
- **BERTRAND LENS:** for the study of interference figures, fixed-focus lens is centerable and mounted in a slideway.
- **STAGE:** diameter 115mm., revolves through 360°, graduated in degrees and reads to 6' with vernier. The top is calibrated in mms. in two directions and is drilled and tapped for an accessory mechanical stage. Stage clips.
- **COMPENSATORS:** two compensators are included; a quarter-wave plate and first order red plate. These fit into a slot above the objective lens.
- **FOCUSING:** coarse and micrometric fine adjustments.
- **STAND:** heavy stand, arm inclines to horizontal position.



1 Iris diaphragm
2 Polarizer
3 Swing-out lever
4 Focusing lock
5 Focusing slide



Condenser and Polarizer

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a ChemEd feature

CHEMICAL PROJECTS

Research Ideas for Young Chemists

Compiled by

JAY A. YOUNG, King's College, Wilkes-Barre, Penna.

JOHN K. TAYLOR, National Bureau of Standards, Washington, D. C.

The Absorption of Hydrogen by Metals

See LEWIS, F. A., *J. Chem. Educ.*, 34, 601 (1957).

Palladium and other transition metals absorb hydrogen. The phenomenon can be studied by using palladium wire as the cathode of an electrolytic cell containing an aqueous solution. Upon electrolysis some of the hydrogen which is produced is adsorbed by the cathode. The cathode can be heated, after removal from the cell, and most or all of the absorbed hydrogen recovered. If recovered in a closed system equipped with a manometer, the quantity of hydrogen can be determined.

Questions:

Does palladium react with hydrogen, forming a hydride, or is the absorption of hydrogen by palladium a physical phenomenon?

Do some of the other transition metals absorb hydrogen, or do they react chemically with hydrogen, or both?

Can you modify the procedure suggested by Lewis to study the interaction between a metal and a gas other than hydrogen?

The Hydrogen Organ

See EDDY, R. D., *J. Chem. Educ.*, 36, 256 (1959).

Very few investigations will approach this one in dramatic audible sounds and spectacular pyrotechnics. Hydrogen, contained in a vessel of suitable shape, is allowed to escape through a very small hole in the top of the vessel. The escaping hydrogen is ignited. As it escapes, air, entering through a large opening in the bottom of the vessel sets up sound vibrations which culminate in a sharp, loud noise when the mixture of air and hydrogen, in the vessel, reaches the proper proportions.

Question:

In his article, Dr. Eddy states that the pitch of the siren-like sound, which is noted before the culminating rapid combustion, depends upon the changing average velocity of the gas molecules within the vessel as the hydrogen is replaced by air. Can you confirm, or disprove, this statement?

Hydrogen Peroxide

See STONE, C. H., *J. Chem. Educ.*, 21, 300–2 (1944).

Twenty-six different reactions, each involving hydrogen peroxide, are described. For some, equations are given. The experimental set-up in each case is simple, requiring only ordinary apparatus. Some of the twenty-six are the catalyzed decomposition of hydrogen peroxide, the formation of perchromate ion, the formation of lead dioxide, the oxidation of lead sulfide, and the oxidation of iodine to iodic acid.

Question:

Select any one of the twenty-six examples described in the article and carry out the operations described. Then, confirm the validity of the equation given by the author to account for the phenomena you observe; or, if no equation is given, suggest a plausible equation and verify it.

Sodium Perborate in the Chemical Laboratory

See ALLEN, C. F. H., AND CLARK, J. H., *J. Chem. Educ.*, 19, 72 (1942).

Many oxidizing agents are hazardous, since they often tend to oxidize reducing agents when such a reaction is unexpected. The heat generated in an unplanned exothermic reaction can be extremely troublesome. Of the known controllable oxidizing agents, sodium preborate (as ordinarily purchased it contains water of crystallization), $NaBO_3 \cdot 4H_2O$, is probably the most tractable. It can be used in place of sodium peroxide, for example, in many, though not all, reactions in which this oxidizing agent is used.

Questions:

Can sodium perborate be used as a safe source of oxygen, in place of potassium perchlorate or hydrogen peroxide? If so, what reactions take place in the decomposition of sodium perborate to yield elemental oxygen?

In addition to the two reactions mentioned by the authors the oxidation of chromite to chromate and the cleavage of an alpha-diketone, in what other reactions can sodium perborate be substituted for sodium peroxide?

Can you find any reactions which ordinarily use an oxidizing agent other than sodium peroxide, for which sodium perborate can be satisfactorily substituted?

Is sodium perborate suitable as a reagent in any reactions in which its oxidizing properties are not paramount? Thus, is the alkaline character of sodium perborate particularly useful in a selected reaction, for example? Or, as another example, will the perborate ion act as a ligand in the formation of complex ions or compounds?

(*Continued on page A46*)

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Peristaltic Pump with air motor incorporates all the advantages and performance features of the standard model—but adds a new element of versatility. Explosion proof air motor can operate in locations where no electrical facilities exist. Has needle valve for precise control.

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(continued from page A44)

CHEMICAL PROJECTS

Genuine and Synthetic Rubies and Sapphires

See ALEXANDER, A. E., *J. Chem. Educ.*, **23**, 418–22, 459 (1946).

Molten alumina, when allowed to accumulate, drop-wise, on a relatively cool surface, will form a gem-like substance. Small amounts of contaminants, added to the aluminum oxide before it is melted, will yield boules which are quite similar to genuine gems. The procedure to be used is described in sufficient detail so that an enterprising student can make his own synthetic rubies or sapphires. Criteria for distinguishing between synthetic and genuine gems are discussed.

In place of the oxygen-hydrogen torch suggested, an oxygen-fuel gas torch will work satisfactorily. Students who use the Verneuill furnace described, which incorporates the torch, should interpose a safety shield between themselves and the furnace during the operation of the furnace.

Questions:

Prepare a synthetic ruby or sapphire by the method described. Can you distinguish your gem from a genuine gem?

Can any other gems, in addition to rubies and sapphires, be prepared using the Verneuill furnace, or a modification of this furnace?

Can you make a synthetic star sapphire, or other gem with a distinguishing interior marking?

Are there any other methods which you can devise for the preparation of a synthetic gem or semiprecious stone? If successful, how can your synthetic product be distinguished from the genuine, natural substance?

The Recovery of Tin from Tin Cans

See OESPER, R. E., *J. Chem. Educ.*, **20**, 406 (1943).

Although many "tin" cans used for the storage of food today are made of steel coated with a protective, organic, lacquer, tin-coated steel cans can be easily obtained. The tin coating can be removed by any one of several oxidation processes which do not affect the steel base. The tin, in oxidized form, can then be reduced to the metallic state and the tin, originally on the can, can thus be recovered and re-used. (During World War II, scarce tin metal was recovered and reused in ton quantities.) One method for the oxidation and subsequent reduction of the tin on a tin can is described in the article.

Questions:

Professor Oesper states that approximately 75% of the tin on a tin can is recoverable by the procedure he describes. Can you confirm this statement?

What other procedures can you find, or devise, for the recovery of the tin coating on a tin can? What per cent recovery can be effected by your method?

Determine the purity of the tin recovered by Oesper's suggested procedure, or by another procedure which you have chosen. Are some, or all, of the impurities present in the recovered tin due to the impurities in the original metal coating, or were they introduced by your procedure?

Can you verify that the reactions cited by Oesper in his article are those which in fact take place?

In the procedure described by Oesper, the tin is oxidized and the steel remains substantially unaffected. Can you devise a procedure in which the steel is oxidized and the tin remains, unaffected? If so, determine the reactions which occur, and verify your determinations by further laboratory work. If not, suggest reasons for this result, and confirm your suggestions by further laboratory work.

Equivalent Weight by Reduction of Copper Oxide—A Modified Procedure

See MURPHY, D. B., *J. Chem. Educ.*, **27**, 463 (1950).

Copper oxide can be reduced to copper by hydrogen, as is well known, and from the quantitative data obtained in such an experiment, the equivalent weight of copper can be determined. However, in the hands of an inexperienced student, this experiment is hazardous. Murphy suggests that ammonia, instead of hydrogen, be used. Two test tubes joined by a drying tube and short lengths of tubing, one containing the copper oxide and the other a mixture of ammonium chloride and calcium oxide, are heated. The ammonia which is generated in one test tube passes into the other test tube and there reacts with the copper oxide. This procedure is not hazardous, and good results can be obtained when sufficient care is taken in the weighings and in the manipulative steps.

Questions:

Will any gases in addition to ammonia, and other solids, in addition to copper(II) oxide, react when the procedure suggested by Murphy is used? What products are formed in such reactions?

Identify other potentially hazardous operations described in one or more laboratory manuals, and devise an alternate procedure which is non-hazardous.

What products are formed when ammonia reacts with copper(II) oxide?

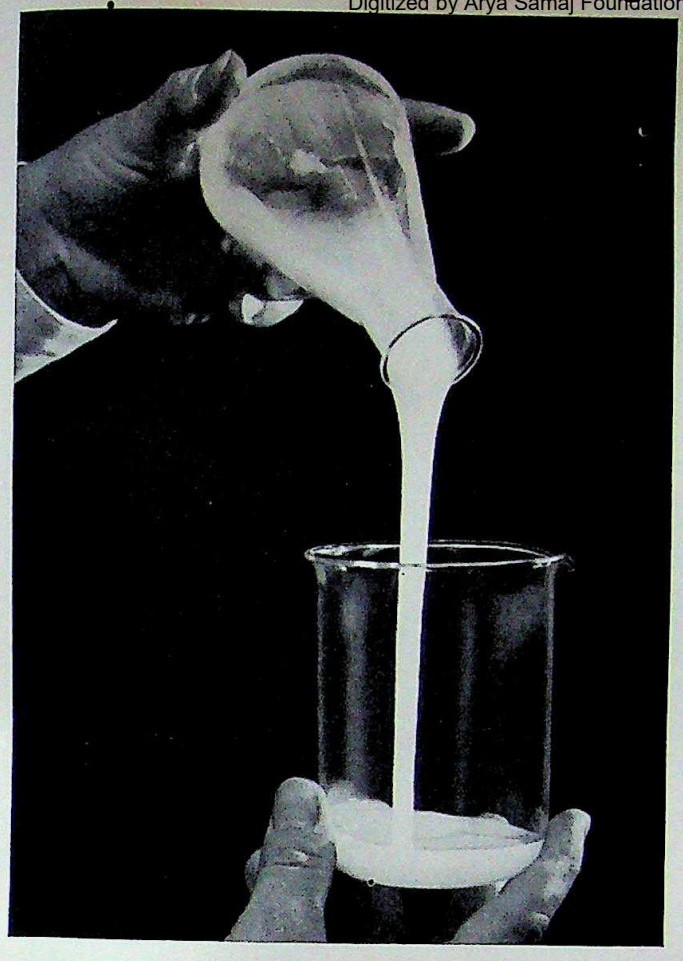
What other compounds can you find which are also reduced by ammonia, when the procedure described by Murphy is used?

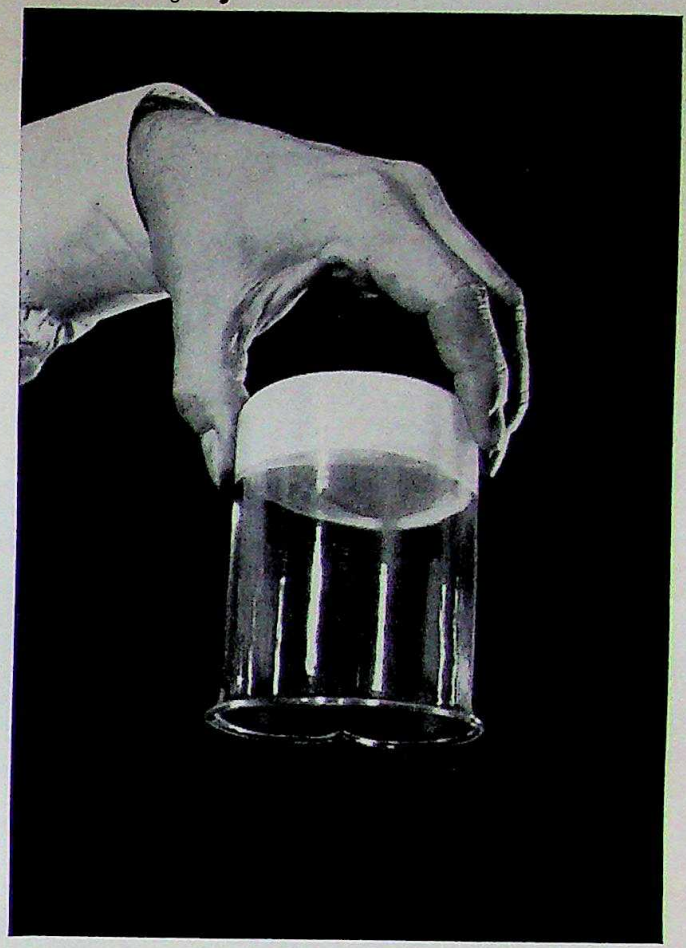
NOTE: The discussion by J. NASH, *J. Chem. Educ.*, 21, 46 (1944) on the reduction of iron(III) oxide to iron is recommended to students who wish to study these questions.

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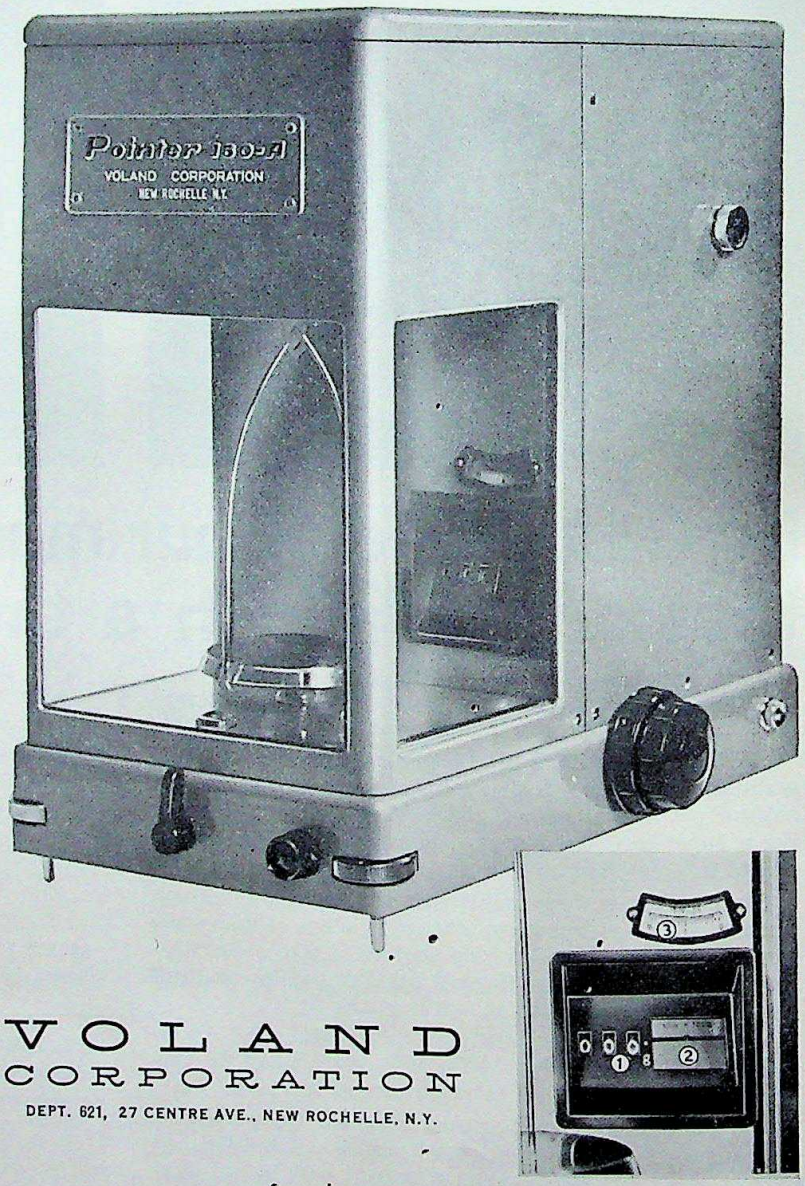
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Luminescent Compounds, i. e., Phosphors

A Chem Ed TESTED DEMONSTRATION

Submitted by: H. R. Tietzie, New Castle University College, New South Wales, Australia

Checked by: David B. Moss and Dale Dreisbach, Hiram College, Hiram, Ohio

DETACH PAGE BY CUTTING ALONG THIS LINE—INDIVIDUAL DEMONSTRATIONS MAY BE CUT APART AND PASTED ON 5 X 8 CARDS

STRONTIUM SULFIDE PHOSPHOR

Provide 10 g $SrCO_3$, 10g roll sulfur, 0.05 g KCl, 0.05 g NaCl and 0.04 g $MnCl_2.4H_2O$. Thoroughly mix the above ingredients by grinding them together in a mortar. Fire the mixture for about $^1/_2$ hour at 800°C. The resulting product has a yellow luminescence.

CADMIUM CHLOROPHOSPHATE PHOSPHOR

Dissolve 27 g $CdCO_3$ in 30 ml conc HCl and 40 ml distilled water, and filter. Mix the filtrate with 69 g $CdHPO_4$ and 2.6 g $MnHPO_4$, and dry the mixture slowly under a hood. Grind the mixture, and heat in a furnace for $^1/_2$ hour at 600°C. Regrind and heat for $^1/_2$ hour at 800°C. This last operation should be repeated. After cooling, wash the mixture free from Cl^- with distilled water, and dry. The resulting product has a red luminescence.

ALTERNATE METHOD

Suggested by: J. F. Ross and D. T. Hurd of General Electric Company

Mix either 241 g $CdNH_4PO_4.H_2O$ or 400 g $Cd_2P_2O_7$ with 46.5 g $CdCO_3$, 31 g $CdCl_2$ and 6.6 g $MnCO_3$. ($Cd_2P_2O_7$ can be precipitated from $CdCl_2$ and $Na_4P_2O_7$ solutions. $MnCO_3$ can be precipitated from $MnCl_2$ and Na_2CO_3 solutions.) Pulverize to mix, and fire in furnace for 45 min. in covered boats or a tray at 1000°C.

The resulting phosphor is bright orange-yellow.

A REACTION TUBE FOR SODIUM AND CHLORINE

A Chem Ed TESTED DEMONSTRATION

Submitted by: Robert Barnard, Montana State College, Bozeman

Checked by: Roger Wheaton, Michigan State University, East Lansing

PREPARATION

Prepare several reaction tubes by bending 10 mm Pyrex tubing into slightly less than a "V" shape with each arm approximately 10–15 mm long.

Prepare cubes of sodium metal (under a hydrocarbon) which will slide into the reaction tube.

Additional materials include: a source of chlorine gas, bunsen burner, and a sodium hydroxide trap.

Clamp the reaction tube between two ring stands, connecting one end of the tube to the source of chlorine. Dry the sodium by pressing it between a piece of absorbent paper and drop it into the open end of the reaction tube. Shake the tube if necessary to place the sodium at the bottom of the "V." Connect the open end of the tube to a sodium hydroxide trap.

DEMONSTRATION

The sodium may now be heated and will display a shiny metallic surface. Remove the heat and pass chlorine into the system (gently). The metal will react immediately. Intense heat and light will be generated. Shut off the flow of chlorine and disconnect the trap to prevent syphoning. The tube will break at the area of reaction and white sodium chloride may be observed.

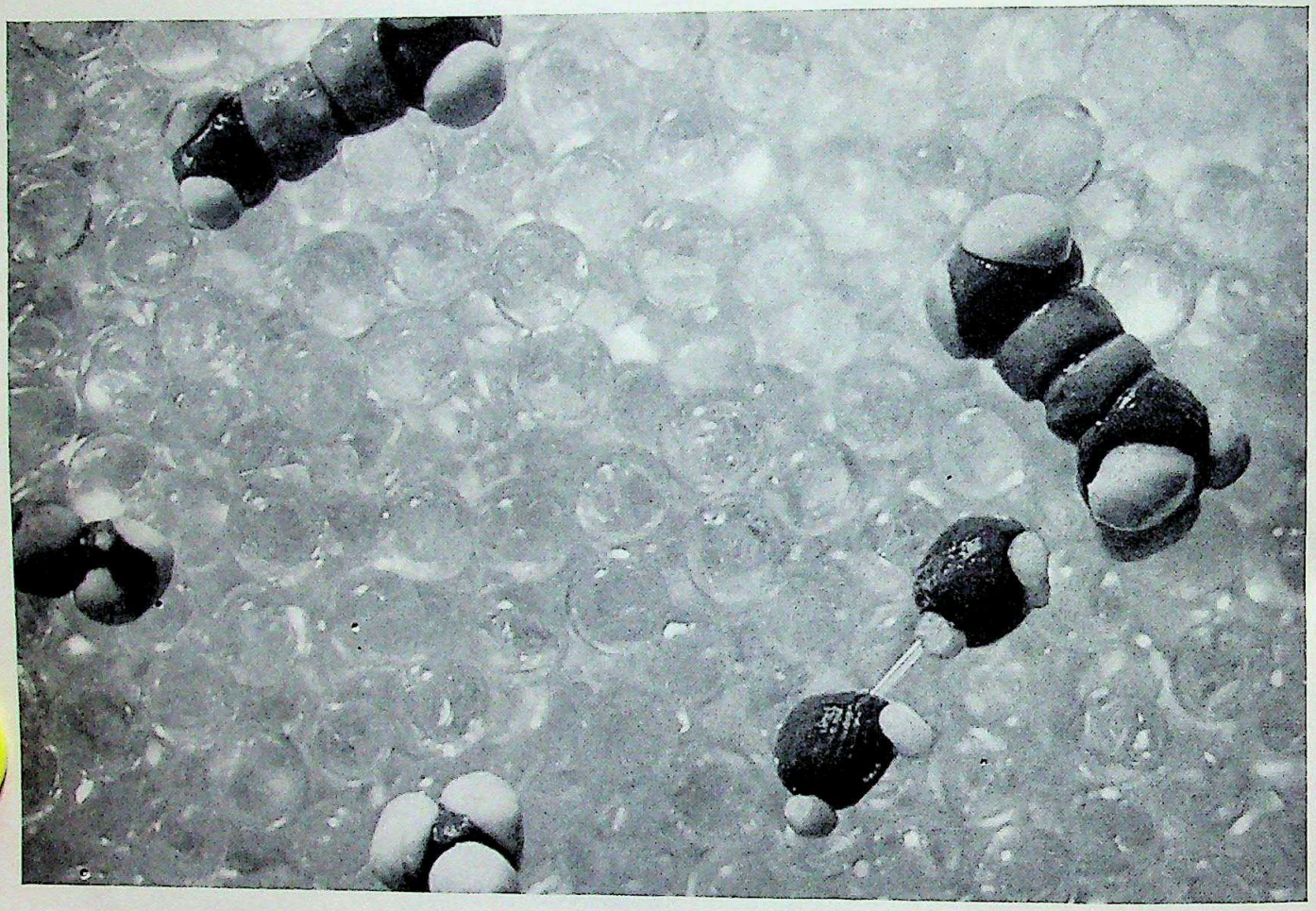
REMARKS

(The original demonstration was suggested in "Experiments in General Chemistry" by Gaines, Woodriff, Binder, Johansson, C. V. Mosby Co., St. Louis, Mo., 1951.)

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from abstract ideas . . . fundamental knowledge at Esso Research



Existence of the "cage" effect, an important concept in solution kinetics, has been confirmed directly by two Esso Research chemists, Dr. Richard K. Lyon and Mr. Donald H. Levy.

The Franck-Rabinowitch cage effect is the reverse of the diffusion controlled recombination reaction. Two highly reactive species, A and B, may react with each other so readily that the rate of reaction of an initially separate pair A and B is controlled by their diffusion towards each other. Conversely, if A and B are produced very close together (for example by the reaction $AN_2B \rightarrow N_2 + A + B$), they may react with each other before they can diffuse apart. Figuratively, as depicted in the illustration, the solvent molecules form a cage holding the reactants together. Numerous observations have been explained by invoking this "cage" effect with varying degrees of certainty.

In the experiments at Esso Research, mixtures of azomethane and d_6-azomethane were photolyzed both in gas phase and in isooctane solution. Primary steps formed CH_3 and CD_3 radicals, followed by hydrogen abstraction to methane or recombination to ethane.

Gas phase recombination occurs randomly among methyl radicals forming ethane in proportions such that $(CH_3 CD_3)^2 / (C_2H_6)(C_2D_6) = 4$. In solution, however, no detectable CH_3CD_3 forms, but appreciable C_2H_6 and C_2D_6 do form, experimentally proving the "cage" effect.

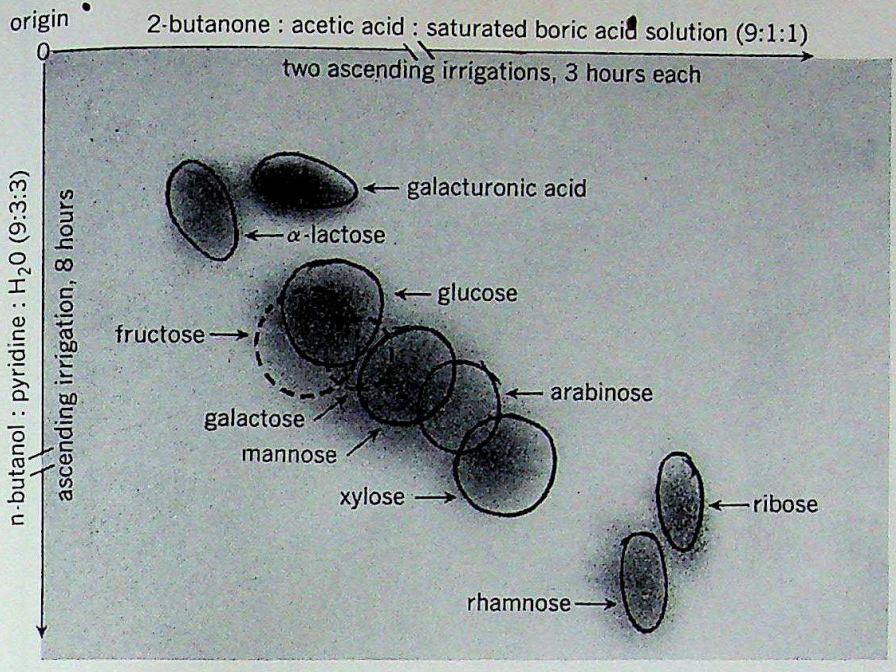
Separate experiments have shown "cage" effects occurring in high pressure gas phase, the diffusion coefficient being somewhat larger than in solution. These hitherto unknown "cage" effects may have a marked influence on high pressure gas phase reaction kinetics. Consideration of this effect in both high pressure gas phase and solution reactions may have great significance in determining the optimum conditions for new or existing chemical processes.

. . . adapted from the scientists' notes
Esso Research and Engineering Company
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naked-eye colorimetry in paper chromatography . . . showing right from wrong . . . picturing slow neutrons



Delicious colors with sugars

No colorimeters, no spectrophotometers are required to do paper chromatography. A ruler is the only measuring instrument. Despite the unimposing contribution that paper chromatography can make to the size of one's capital budget, the technique grows ever more popular. Now a contemptible pittance—a ridiculous $4.65—buys 25 grams of *p-Anisidine Hydrochloride* (EASTMAN 8615) and permits the purchaser to let on that he uses colorimetry (naked-eye type) in his paper chromatography.

We were going to offer with our compliments a color photograph of this chromatogram as it looked when wet and fresh. The thought to do so came after reading the account (*J. Chem. Soc., 1950*, 1702) of how p-anisidine hydrochloride turned up from a systematic hunt for a universal reagent that would yield a specific color with each particular class of sugar or methylated sugar. It said that aldohexoses give "green-brown," ketohexoses "brilliant lemon yellow," methyl aldopentoses "emerald green," uronic acids "cherry red"—all delicious colors like that.

We have decided not to do it. We fear that our photography would be blamed if the colors in the photograph seemed drabber than the verbal designations. Remember that the paper chromatographers' eager pursuit of color in their working lives leaves them more impressionable in this respect than other people. Let them better order a little bottle of EASTMAN 8615 and impress themselves privately.

We also have *Aniline Hydrogen Phthalate* (EASTMAN 8608), which is also well spoken of for the same general purpose. "Excellent colours" with the methylated sugars are mentioned, with detectability down to 1-5 μg.

We also have a new catalog, List No. 43, which tells about some 4,000 other EASTMAN Organic Chemicals obtainable from Distillation Products Industries, Rochester 3, N. Y. (Division of Eastman Kodak Company).

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We have another pedagogical suggestion, which you may think good or bad. Take a paper turned in by a student in the class and copy it on VERIFAX Transparent Sheeting, omitting his name to avoid embarrassment or jealousy as the case may be. Project it and mark it up right then and there on the projector. Brings the difference between right and wrong close to home in a convincing manner.

Eastman Kodak Company, Business Photo Methods Division, Rochester 4, N. Y. can place VERIFAX Transparent Sheeting in your hands right away. If you don't even have a VERIFAX Copier, somebody ought to look it up under "Photocopy Machines" or "Duplicating Machines" in the Yellow Pages of the telephone directory.

The Sun play

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You do it by a triple play: thermal neutrons activate ^{10}B to emit alphas, which scintillate ZnS(Ag), which gives off visible light that exposes the film. For sharper images at the expense of longer exposure time, you can use a neutron activation technique involving an appreciable half-life. There are gadolinium, which works by an n,γ reaction, and dysprosium, which works by β decay. Expose such a neutron converter sheet without the film and then quickly pull it out of the neutron flux and put it in contact with the film.

As to which film, we suggest you first read J. App. Phys., 33, *48 and* Nucleonics, *July, 1962, pp. 60 and 61, and then ask for a film recommendation from Eastman Kodak Company, X-ray Division, Rochester 4, N. Y. Nice big sheets of gadolinium are not stocked by most neighborhood hardware merchants nor by us. Maybe your best bet after all is the ^{10}B scintillator.*

A prominent role in all this has been played by a gentleman named Kuan-Han Sun, who once worked for us before his interest turned from non-silicate optical glasses to nucleonics. Married one of our x-ray researchers and took her off with him. Lovely gal whose name was Laura McGillivray.

Eastman Kodak Company ads like this have been appearing for 10 years. They suggest that we make a wide variety of products. Possibly you have at one time or another thought of buying one but, not knowing how to go about it, have said, "The devil with it." Are you interested enough to send for a pocket reference book that may help you and us achieve mutually beneficial contact? If so, address Eastman Kodak Company, Dept. 8, Rochester 4, N.Y. It is a tiny bit out of date, but that can't be helped. (Everybody dies a little each day.)

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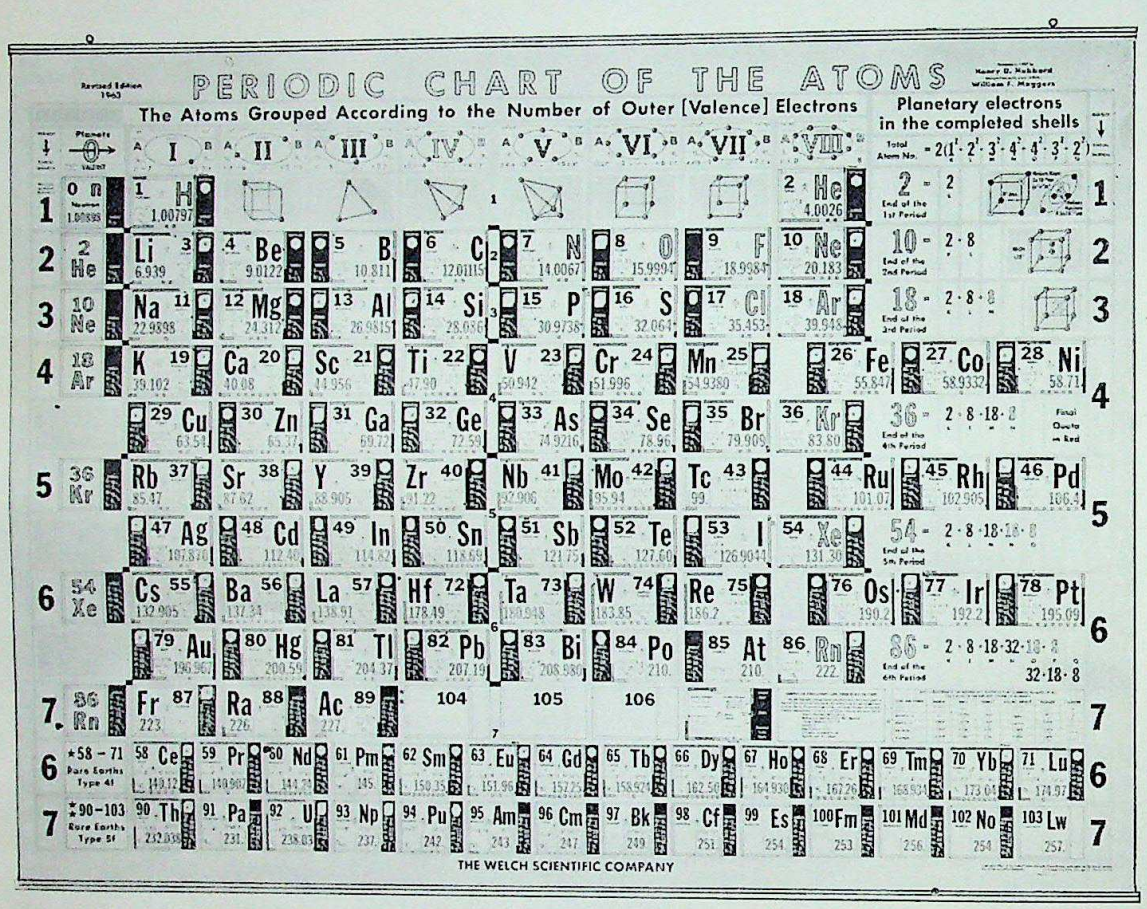
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Chem Ed

EDITORIALLY SPEAKING

Janus—the god of the forward and backward look—has this month for his memorial. The attitudes he symbolizes are appropriate for the start of a new year. We hope indulgent readers will allow us a few comments of counting up, taking inventory and anticipating on this page one of volume 40.

Volume 39 is the fattest set of twelve issues THIS JOURNAL has produced. Readers who enjoy counting things (and we get about twenty manuscripts a year from people who have counted *something* chemical!) will discover that their 1962 issues contained nearly 50 pages more editorial material than in previous years! The Tables of Contents listed about 250 article titles in addition to the regular monthly features: Instrumentation, TOPS, Tested Demonstrations and Projects. About 200 books were reviewed. Four symposia were presented. The ongoing series of Textbook Errors added its annual quota of six; eleven items in the newly introduced Flash of Genius series appeared.

Advertising in the JOURNAL showed a healthy growth during last year. Readers do not need a complicated economic analysis to realize that the only way they can see their same 1958 subscription price buy more JOURNAL in spite of increased production costs is to maintain a fairly consistent ad-to-ed-content, balance. What readers apparently do need to be told is that advertisers want to know where their message is read. Adding the phrase, "I note from your ad in J. CHEM. EDUC.," when writing for information would be an excellent and most helpful resolution for friends of THIS JOURNAL in 1963.

We are encouraged by the growth of our list of subscribers in 1962. More than 1,700 new names were added to bring the total to a high of 16,300. We earnestly hope that these new friends will not be disappointed. Keeping readers interested in the content of THE JOURNAL is the editor's major concern and problem. There are bound to be disappointments. Especially is this becoming increasingly true among the authors of papers submitted. In the past year, the editor's office received about 500 manuscripts. The only possible answers to the inevitable arithmetic are a higher rejection rate, and regrettably longer delays before publication of accepted papers.

Readers may be interested in looking ahead to features planned for 1963. The issue next month will contain articles discussing Ionic Crystal Structures, Titration Errors, Recent Developments in Glass, and the Gmelin Institute.

March will be an inorganic issue. Reviews will treat Graphite, Superoxides, Phosphorous Halides, Organometallics, Electronic Spectra of Transition Metal Complexes, and other themes.

April is shaping up with emphasis on organic chemistry: Diene Iron Tricarbonyl Complexes, Multicenter Mechanistic Pathways, Ribonucleic Acid and others.

Further in the future but definitely planned for the coming year are: Lasers—Potential Chemical Tools (including a description of experiments for the undergraduate laboratory); HO_2—The Furtive, Unobservable Theoretical Necessity; and more physical chemistry laboratory experiments on interpretation of spectra. Materials prepared under the aegis of the NSF sponsored Advisory Council on College Chemistry should start to appear in 1963.

The "Living Textbook of Chemistry" thus attains its forties. The famous—or infamous—39 has been passed. We thank readers for the confidence of their support and hope that the volume we now begin will deserve it too.

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Conventions Defining Thermodynamic Properties of Aqueous Ions and Other Chemical Species

Richard M. Noyes
University of Oregon
Eugene

Chemical thermodynamics is concerned with changes in properties associated with changes in state resulting from chemical reactions. Since only changes in the values of most thermodynamic properties are of interest, the absolute values of these properties are unimportant.

In such a situation, it is customary to adopt a *convention* arbitrarily defining the value of a property for some specified reference system. Once such a convention has been adopted, the value of the property is also defined for any other system provided it is possible to measure the change in the property associated with the change in state between the two systems.

A familiar non-chemical example involves the potential energy of an object in the earth's gravitational field. For different types of calculation, this potential energy could conveniently be assigned the value zero at the center of the earth, at sea level, at some reference point in the laboratory, or at an infinite distance from the earth. These conventions lead to very different absolute values for the potential energy of the object in any specific situation, but consistent application of any of these conventions will give the same value for the change in potential energy associated with any change in position of the object.

A chemical reaction can conveniently be generalized by the equation

$$\sum_i n_i \mathrm{R}_i \rightarrow \sum_j n_j \mathrm{P}_j \qquad (1)$$

where the R's are reactants and the P's are products. The n's are rational numbers whose relative values are determined by the stoichiometry of the reaction. The equation must be balanced with respect to elements and charges by methods familiar to all chemists, and sufficient properties like temperature and pressure must be specified so that the state of each of the species in equation (1) is uniquely defined.

If proper chemical conventions are adopted, the values of properties like enthalpy, entropy, and free energy can be tabulated for species in specified states so that quantities like ΔH, ΔS, and ΔF can be computed for any reaction like equation (1) provided tabulated data are available for all of the species in the equation. Such tabulations based on the same set of conventions have been prepared for many chemical species at 25°C and 1 atmosphere by the Bureau of Standards[1] and by Latimer.[2]

It is very useful to tabulate values based on a convention provided everybody understands the convention. Most persons using these tables for thermodynamic calculations do indeed know the conventions and use them consistently for the problems of interest. Probably comparatively few of them realize that the conventions with regard to aqueous ions are not internally consistent for certain types of reactions and that an uncritical use of tabulated data can lead to violations of some of the basic equations of thermodynamics.

The purpose of this paper is to summarize the conventions presently used to tabulate thermodynamic properties of chemical species, to show the reaction types for which these tabulations are and are not applicable, and to suggest alternative conventions that could extend the applicability of the tabulations.

Conventions for Observable Chemical Systems

Tabulations of thermodynamic properties[1, 2] list the quantities ΔH_f°, ΔF_f°, and S°. Conventions defining these quantities are:

Convention 1. **The quantity ΔH_f° at any temperature is the enthalpy change per mole of species formed in its standard state from the elements in the standard states in which they exist at the same temperature.** Of course ΔH_f° will be zero for an element in this standard state.

Convention 2. **The quantity ΔF_f° is the free energy change for formation from the elements under the same conditions as in convention 1.**

Convention 3. **The quantity S° at any temperature is the molar entropy in the standard state provided the entropy of a perfect crystal of that species is defined to approach zero as the absolute temperature approaches zero.** The value of S° may be based on thermal measurements that include heat capacity data extended to very low temperatures; it may also be based on computations that employ the principles of statistical thermodynamics. The two methods of assigning entropies give the same results to within the accuracy with which they can be compared.

The above conventions refer to standard states. For a liquid or crystalline solid (designated by l and c, respectively), the usual standard state is pure substance at 25°C and 1 atmosphere pressure.

For a gas (designated by g), the standard state at 25°C has the same enthalpy, entropy, and free energy as one atmosphere of a hypothetical gas identical with

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[1] "Selected Values of Chemical Thermodynamic Properties," Circular of the National Bureau of Standards No. 500, U. S. Government Printing Office, Washington, D. C., 1952.

[2] LATIMER, W. M., "The Oxidation States of the Elements and Their Potentials in Aqueous Solutions," 2nd ed., Prentice-Hall, Inc., New York, 1952.

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the real gas at very low pressures but obeying the ideal equation of state during compression. Since most gases at one atmosphere fugacity have pressures very close to one atmosphere, and since thermodynamic properties of condensed phases are not very sensitive to small changes in pressure, a reaction in which reactants and products are all in their standard states can be regarded as a reaction at constant pressure for the purpose of relating thermal effects to changes in thermodynamic properties like ΔH.

The designation *aq* indicates a dilute aqueous solution. In the standard state at 25°C and 1 atmosphere pressure, the solute has the same enthalpy as in an infinitely dilute solution. The free energy and entropy of the solute in this standard state are those computed for a hypothetical ideal solution at unit activity if the activity of solute in a very dilute solution is equal to its molality. This standard state is not necessarily identical with any state that is attainable in reality.

Table 1 contains values at 25°C of thermodynamic properties based on the above conventions for hydrogen, oxygen, sodium, and chlorine and for many of the compounds that can be formed from these elements. The values are taken from the Bureau of Standards listing.[1] Table 1 also contains entries for $C_p°$ which will be discussed later.

These conventions are a little more complicated than the problem of potential energy in a gravitational field discussed previously. If the elements in their standard states at 25° were assigned zero enthalpy and free energy, the values of $H°$ and $F°$ for other species would be the same as the values of $\Delta H_f°$ and $\Delta F_f°$ in Table 1, and people using such tables often treat the entries mentally as though they were $H°$ and $F°$. However, the entries in the table would then violate the equation

$$F° = H° - TS° \tag{2}$$

Because of this difficulty, it is better to call the entries "enthalpies and free energies of formation" rather than "enthalpies" and "free energies."

The entropies in Table 1 are not based on zero values for the elements at 25° because the third law of thermodynamics permits more fundamental expressions that relate entropies of different chemical species to the same scale without the need of a separate convention for each element. Even though the convention for entropy is different from those for enthalpy and free energy, the data for every species in Table 1 will be found to satisfy the equation

$$\Delta F_f° = \Delta H_f° - T\Delta S_f° \tag{3}$$

where $\Delta S_f°$ has the same type of meaning as $\Delta H_f°$ and $\Delta F_f°$.

If a table of such entries is available, standard changes in thermodynamic properties can be computed for a reaction like equation (1) by means of the relations

$$\Delta H° = \sum_j n_j \Delta H_f°(\mathrm{P}_j) - \sum_i n_i \Delta H_f°(\mathrm{R}_i) \tag{4}$$

$$\Delta F° = \sum_j n_j \Delta F_f°(\mathrm{P}_j) - \sum_i n_i \Delta F_f°(\mathrm{R}_i) \tag{5}$$

$$\Delta S° = \sum_j n_j S°(\mathrm{P}_j) - \sum_i n_i S°(\mathrm{R}_i) \tag{6}$$

If the change of state indicated by the equation is carried out, the changes in thermodynamic properties will agree with those computed from tabulated data by means of these equations.

The use of the equations can be illustrated by the reaction

$$2\mathrm{Na}(c) + 2\mathrm{H_2O}(l) \rightarrow \mathrm{H_2}(g) + 2\mathrm{NaOH}(aq) \tag{7}$$

Since sodium hydroxide is a strong electrolyte, the last entry could be replaced by $2\mathrm{Na^+}(aq) + 2\mathrm{OH^-}(aq)$. Application of data from Table 1 gives

$$\Delta H° = -224.472 + 0 + 136.6348 - 0 = -87.837 \text{ kcal/mole} \tag{8}$$

$$\Delta F° = -200.368 + 0 + 113.3804 - 0 = -86.988 \text{ kcal/mole} \tag{9}$$

$$\Delta S° = 23.8 + 31.211 - 33.432 - 24.4 = -2.8 \text{ cal/mole deg}$$

$$= (\Delta H° - \Delta F°)/T \tag{10}$$

The self-consistency of the conventions is illustrated by the fact that these data satisfy the equation

$$\Delta S° = \frac{\Delta H° - \Delta F°}{T} \tag{11}$$

Any other balanced equation based on the entries in Table 1 could be used to show that these entries are self-consistent.

The above conventions are not sufficient to permit application to all conceivable equations for reactions. Thus conventions 1 and 2 effectively assign values to thermodynamic properties for each element and assume that the nuclear properties of that element are unaffected by the reaction.

Similarly, since the elements in their standard states are electrically neutral, these conventions are only sufficient for application to equations such that each side is electrically neutral. Even though a solution of a strong electrolyte like $\mathrm{NaOH}(aq)$ may be dissociated into ions, the total concentrations of positive and negative charge in the solution must be equal. Any equation for which these conventions are sufficient must satisfy this requirement of electrical neutrality even if the equation as written includes ions that do not enter into the reaction.

Table 1. Thermodynamic Properties of some Observable Chemical Species at 25°C[a]

Substance	State	$\Delta H_f°$ kcal/mole	$\Delta F_f°$ kcal/mole	$S°$ cal/mole deg	$C_p°$ cal/mole deg
H	*g*	52.089	48.575	27.3927	4.9680
H_2	*g*	0.000	0.000	31.211	−6.892
O	*g*	59.159	54.994	38.4689	5.2364
O_2	*g*	0.000	0.000	49.003	7.017
O_2	*aq*	− 3.8			
O_3	*g*	34.0	39.06	56.8	9.12
OH	*g*	10.06	8.93	43.888	7.141
H_2O	*g*	− 57.7979	− 54.6357	45.106	8.025
H_2O	*l*	− 68.3174	− 56.6902	16.716	17.996
H_2O_2	*g*	− 31.83			
H_2O_2	*l*	− 44.84			
H_2O_2	*aq*	− 45.68			
Cl	*g*	29.012	25.192	39.4569	5.2203
Cl_2	*g*	0.000	0.000	53.286	8.11
Cl_2	*aq*	− 6.0			
HCl	*g*	− 22.063	− 22.769	44.617	6.96
HCl	*aq*	− 40.023	− 31.350	13.16	−30.0
$HClO_3$	*aq*	− 23.4			
$HClO_4$	*aq*	− 31.41			
Na	*g*	25.98	18.67	36.715	4.9680
Na	*c*	0.000	0.000	12.2	6.79
Na_2	*g*	33.97	24.85	55.02	
Na_2O	*c*	− 99.4	− 90.0	17.4	16.3
NaOH	*c*	−101.99			19.2
NaOH	*aq*	−112.236	−100.184	11.9	
NaCl	*g*	− 43.50			
NaCl	*c*	− 98.232	− 91.785	17.30	11.88
NaCl	*aq*	− 97.302	− 93.939	27.6	
$NaClO_3$	*aq*	− 80.78	− 62.21	53.4	
$NaClO_4$	*aq*	− 88.69	− 65.16	57.9	

[a] These entries are based on conventions 1–3 and are applicable to reactions of type A.

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It is convenient to summarize these requirements and to classify types of reactions to which different conventions may be safely applied. *Reactions of type A* involve no change in nuclear structure or in isotopic composition; they involve no charged species other than aqueous ions; and both sides of any equation are electrically neutral.

Equation (7) is an example of a reaction of type A. Although very many chemical reactions belong to type A, other situations are also of interest. Additional or alternative conventions must be adopted if they are to be treated. Some of the possibilities are considered in the following sections.

Nuclear Reactions

Reactions of type B involve some change in nuclear structure. An example is

$$^{1}_{1}\mathrm{H} + {}^{7}_{3}\mathrm{Li} \rightarrow 2\ {}^{4}_{2}\mathrm{He} \qquad (12)$$

Such a reaction cannot be treated by means of conventions 1–3. Physicists talk about the energy changes associated with such reactions, but the necessary conventions must be based on the energies of fundamental particles or of some specified nucleus such as oxygen-16. Often these reactions are carried out under conditions such that it is impossible to talk about temperature or entropy, but reactions of thermal neutrons in a uranium pile and of ions in a hot plasma would lend themselves to treatments like those of chemical thermodynamics. Any such treatment would require different conventions and would be outside the scope of this paper.

Isotope Fractionation Reactions

Reactions of type C involve change in isotopic composition of the atoms in one of the chemical forms of some element. Convention 3 defines the entropy of a species so as to neglect the mixing of isotopic species of the same element. Such a convention is satisfactory for application to any reaction such that all species containing that element have the same isotopic distribution. If that distribution changes during reaction, additional entropy effects must be considered.

If X_k is the mole fraction of an isotopic species, and if only one atom of an element is present per mole of a chemical substance, a treatment that accounted for isotope effects would increase the entropy of that substance in Table 1 by an amount

$$S_{\text{isotope}} = -R\sum_k X_k \ln X_k \qquad (13)$$

Of course, $\sum_k X_k = 1$.

As an example, natural chlorine contains 75.4% of ^{35}Cl and 24.6% of ^{37}Cl. Hence the entropies of Cl(g) and of HCl(g) in Table 1 would be increased by 1.109 cal/mole deg if this fact were considered.

If any chemical species contains more than one atom per mole, the entropy corrections depend upon whether the atoms are indistinguishable in position as in N_2 or are distinguishable as in NNO.

Although isotopic fractionation chiefly affects entropy values, enthalpy values of some compounds can also be influenced by isotopic fractionation of the lighter elements.

During most chemical reactions, the isotopic composition of an element is virtually the same in all chemical species containing that element, and the simplest procedure is to neglect the entropy of isotopic mixing. However, it is well to remember that such neglect is involved in convention 3 and in Table 1.

Conventions for Reactions of Gaseous Ions

Reactions of type D involve gaseous ions and may also involve gaseous electrons. They involve no nuclear or isotope fractionation reactions, and any aqueous ions must satisfy the electroneutrality requirement for reactions of type A.

Examples are

$$\mathrm{Na}(c) \rightarrow \mathrm{Na}^+(g) + \mathrm{e}^-(g) \qquad (14)$$

$$\mathrm{Na}(g) + \mathrm{H}^+(g) \rightarrow \mathrm{Na}^+(g) + \mathrm{H}(g) \qquad (15)$$

In order to treat such reactions, an additional convention is necessary.

Convention 4. **The energy of a gaseous electron is zero except for its kinetic energy.**

According to this convention, the molar enthalpy of an electron gas is $(5/2)RT$, and the difference in energy of a positive ion from that of an atom is equal to the minimum energy necessary to cause ionization.

Standard tabulations of thermodynamic quantities[1, 2] assign enthalpies of formation to gaseous ions in this way but do not state convention 4 specifically. They do not make any attempt to assign entropies or free energies to these ions. However, the entropy of a monatomic species depends only on the mass and the distribution of electronic energy levels. Since the mass of an ion is insignificantly different from that of the parent atom, entropies of gaseous ions differ from those of atoms only by easily calculable terms involving electronic partition functions. Free energies of formation of gaseous ions can then be defined to give consistency with equation (11) for any reaction.

The thermodynamic properties of gaseous electrons can also be calculated by standard equations of statistical thermodynamics with application of convention 4.

Table 2 lists thermodynamic properties of electrons and of some gaseous ions derivable from the elements of Table 1. The entries are based on all four of the conventions that have been introduced. They satisfy equation (3), and application to a balanced equation will be self-consistent with regard to equation (11).

Table 2. Thermodynamic Properties of Some Gaseous Ions at 25°C[a]

Substance	State	$\Delta H_f°$ kcal/mole	$\Delta F_f°$ kcal/mole	$S°$ cal/mole deg	$C_p°$ cal/mole deg
e^-	g	1.481	− 0.008	4.994	4.9680
H^+	g	367.088	363.985	26.0153	4.9680
O^+	g	374.609	370.879	37.0109	4.9680
O^-	g	− 13.12			
O_2^+	g	283.1			
OH^-	g	− 76.4			
Cl^+	g	329.349	325.360	40.0215	
Cl^-	g	− 58.3	− 61.3	36.6281	4.9680
Na^+	g	146.015	139.12	35.341	4.9680

[a] These entries are based on conventions 1–4 and are applicable to reactions of type D.

Existing Conventions for Reactions of Aqueous Ions

Reactions of type E usually involve no charged species other than aqueous ions. If they do involve gaseous charged species, such gaseous species must satisfy the

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type of electroneutrality restriction imposed on reactions of type A. No neutrality restrictions are placed on aqueous ions provided the equations are balanced with respect to charge. These equations involve no nuclear or isotope fractionation reactions.

Of course reactions of type A are included in type E. Additional examples not belonging to type A are

$$2Na(c) + 2H^+(aq) \rightarrow 2Na^+(aq) + H_2(g) \quad (16)$$

$$Cl_2(g) + 6OH^-(aq) \rightarrow 5Cl^-(aq) + ClO_3^-(aq) + 3H_2O \quad (17)$$

Although any real solution of ions must contain equal concentrations of positive and negative charge, there is abundant evidence that ions behave independently in sufficiently dilute solution. Hence it is not necessary to write equation (16) to include specifically the negative ions that are also present throughout the entire reaction.

Just as we cannot prepare a solution of sodium ion and measure its properties independent of any negative ions, we cannot get a direct measurement of the contribution of any single type of ion to the thermodynamic properties of an electrolyte solution. However, we can adopt a "bookkeeping" convention that arbitrarily assigns the properties of some one ion. Such a convention can be combined with experimental data to define the properties of all other ions. The following convention is generally applied in order to assign thermodynamic properties to individual ions.

Convention 5a. **Aqueous hydrogen ion in its standard state at any temperature has zero values for the quantities $\Delta H_f°$, $\Delta F_f°$, and $S°$.**

Table 3 presents the values of thermodynamic properties for several aqueous ions derived from the elements of Table 1 and calculated with the use of conventions 1, 2, 3, and 5*a*. A comparison of Tables 1 and 3 will show that the properties for strong electrolytes in Table 1 are the sums of the properties for the individual ions in Table 3.

As was indicated, convention 5*a* is a bookkeeping convention determining how the total value of some property will be divided among constituent ions. Thermodynamic properties listed in Table 3 are never considered to have the same sort of experimental significance as do those in Table 1.

It is less commonly realized that simultaneous adoption of arbitrary conventions for the three quantities $\Delta H_f°$, $\Delta F_f°$, and $S°$ leads to tabulated quantities that violate equation (3). In other words, convention 5*a* over-defines the thermodynamic properties of ions so that some applications not only lack absolute experimental significance but also lack self-consistency in terms of the basic identities of thermodynamics. Some caution is necessary in the application of the entries from Table 3.

Table 3. Thermodynamic Properties of Some Aqueous Ions at 25°C Based on Presently Accepted Conventions[a]

Substance	State	$\Delta H_f°$ kcal/mole	$\Delta F_f°$ kcal/mole	$S°$ cal/mole deg	$C_p°$ cal/mole deg
H^+	*aq*	0.000	0.000	0.000	0.000
OH^-	*aq*	−54.957	−37.595	− 2.519	−32.0
Cl^-	*aq*	−40.023	−31.350	13.17	−30.0
ClO_3^-	*aq*	−23.50	− 0.62	39.0	−18.
ClO_4^-	*aq*	−31.41	− 2.57	43.5	
Na^+	*aq*	−57.279	−62.589	14.4	5.4

[a] These entries are based on conventions 1–3, 5*a*, and 8*a* and are applicable to reactions of types A and E. They cannot be applied consistently to reactions of type G and can only be applied consistently to reactions of type F if convention 6*b* is adopted.

Ionic Reactions Permitting Valid Application

Since the equation for a reaction of type E involves no deviation from electroneutrality except for aqueous ions, the algebraic sum of the charges on such ions is the same on both sides of the equation. For such a reaction, the conventions are self-consistent, and any application to valid data will satisfy equation (11). It will also be susceptible to experimental verification. Such consistency can be demonstrated with any reaction of type E involving the data of Table 3. A more extreme example is provided by the reaction

$$2MnO_4^-(aq) + 5C_2O_4^-(aq) + 16H^+(aq) \rightarrow 2Mn^{2+}(aq) + 10CO_2(g) + 8H_2O(l) \quad (18)$$

Tabulated data[1] for the species in this equation give $\Delta S° = 452.5$ cal/mole deg and $(\Delta H° - \Delta F°)/T = 450.6$ cal/mole deg. The agreement is well within the indicated uncertainties of the data.

Attempted Application to Half-Reactions

When a reaction of type E involves oxidation and reduction of species, it is often convenient for purposes of discussion to break it down into a sum of "half-reactions" involving free electrons.

Reactions of type F involve both electrons and aqueous ions but no other charged species. They involve no nuclear or isotope fractionation reactions.

Examples of such reactions are

$$Na(c) \rightarrow Na^+(aq) + e^- \quad (19)$$

$$ClO_3^-(aq) + 6H^+(aq) + 6e^- \rightarrow Cl^-(aq) + 3H_2O(l) \quad (20)$$

Since half-reactions are used for purposes of balancing equations or for separating reactions at different electrodes in a cell, the state of the electron is usually not specified. Any convention for discussing thermodynamic changes in such reactions will want to introduce the least complication from the presence of electrons. The most obvious one is:

Convention 6a. **The electron in a half-reaction has zero values for $\Delta H_f°$, $\Delta F_f°$, and $S°$.**

An electron in such a state shall henceforth be designated $e^-(0)$. It is possible in principle to define the state $e^-(0)$ so that convention 4 is simultaneously satisfied.

This convention is not self-consistent with conventions 1–5*a*. The inconsistency can be illustrated by applying the data of Table 3 to reaction (19). The results are

$$\Delta H° = -57.279 - 0 = -57.279 \text{ kcal/mole} \quad (21)$$

$$\Delta F° = -62.589 - 0 = -62.589 \text{ kcal/mole} \quad (22)$$

$$\Delta S° = 14.4 - 12.2 = 2.2 \text{ cal/mole deg} \quad (23)$$

$$(\Delta H° - \Delta F°)/T = 17.80 \text{ cal/mole deg} \quad (24)$$

Rossini[3] is one of several authors who have pointed out this lack of consistency. It will be involved in any application of these conventions to a half reaction. The discrepancy could be removed by an alternative convention.

[3] Rossini, F. D., "Chemical Thermodynamics," John Wiley and Sons, Inc., New York, 1950, pp. 374 *ff*.

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Convention 6b. **The electron in a half-reaction has zero values for ΔH_f° and for ΔF_f°, but it has a value of S° equal to half the molar entropy of hydrogen gas, which at 25°C is 15.606 cal/mole deg.**

The reason for such an assignment will become apparent from the discussion below. Although such an entropy assignment seems arbitrary, it is little more so than assigning the value zero. If no other reaction types caused trouble, this modification of convention 6*a* would be sufficient to attain self-consistency in the tabulation of thermodynamic data for chemical reactions. However, the conventions lead to difficulty with another type of reaction also.

Attempted Application to Ion Transport Reactions

Reactions of type G involve net transport of charge between gaseous and aqueous phases. They involve no nuclear or isotope fractionation reactions.

An example is

$$Na^+(g) \rightarrow Na^+(aq) \qquad (25)$$

Of course it is impossible to study the thermodynamics of this process by direct observation. However, the thermodynamic changes associated with reactions like this are of great interest to the understanding of the properties of aqueous ions.

The lack of self-consistency can be illustrated easily for this reaction by applying data from Tables 2 and 3.

$$\Delta H^\circ = -57.279 - 146.015 = -203.294 \text{ kcal/mole} \qquad (26)$$

$$\Delta F^\circ = -62.589 - 139.12 = -201.71 \text{ kcal/mole} \qquad (27)$$

$$\Delta S^\circ = 14.4 - 35.34 = -20.9 \text{ cal/mole deg} \qquad (28)$$

$$(\Delta H^\circ - \Delta F^\circ)/T = -5.30 \text{ cal/mole deg} \qquad (29)$$

The discrepancy is again 15.606 cal/mole deg within experimental error.

This lack of consistency in the conventions was discovered somewhat accidentally during work on the absolute changes in thermodynamic properties associated with processes like reaction (25). Some discussions with Professor Henry S. Frank of the University of Pittsburgh helped greatly to define the nature of the inconsistency. The reasons become apparent from an examination of the conventions presented above.

The data presented in Table 2 and based on convention 4 permit calculation of quantities like ΔH_f° for the species $Na^+(g) + e^-(g)$ as in equation (14). Such quantities satisfy equation (3), and the entries for $e^-(g)$ satisfy equation (2).

The data presented in Table 3 and based on conventions 5*a* and 6*a* permit calculation of similar quantities for the species $Na^+(aq) + e^-(0)$ as in equation (19). Equations (21) to (24) show that use of these conventions will violate equation (3). If convention 6*b* is used instead of convention 6*a*, the thermodynamic changes for formation of $Na^+(aq) + e^-$ satisfy equation (3), but the satisfaction is achieved by assigning properties to the electron that violate equation (2).

Since electrons do not appear on either side of equation (25), the entries from Tables 2 and 3 cannot be combined consistently unless the conventions about electrons in both tables satisfy equation (2) or differ from it in consistent fashion. Strong statistical mechanical arguments can be raised against a modification of convention 4, which provides the basis for the electron entries in Table 2. Although convention 6*a* satisfies equation (2), its use causes all entries for aqueous ions to violate equation (3); use of convention 6*b* permits these entries to satisfy equation (3) but does so by violating equation (2) for electrons in half-reactions. More fundamental changes in convention will be necessary if tabulated data are to be applied to transport processes like equation (25).

The Electrochemical Conventions

If a modified convention is to be adopted for aqueous ions, it should recognize the electrochemical conventions of long standing in discussing the potentials of single electrodes.

The potential of a chemical cell is the potential of the right electrode relative to the left, and the reaction of the cell is the chemical process that takes place when current passes so that reduction takes place at the right electrode. For this situation

$$\Delta F^\circ = -z\mathfrak{F}E^\circ \qquad (30)$$

where E° is the potential of the cell when all reactants and products are in their standard states, $\mathfrak{F}$ is the Faraday constant, and ΔF° is the standard free energy change (in joules per mole) for the cell reaction associated with passage of z moles of electrons.

Since the absolute potential of a single electrode cannot be measured as accurately as the difference in potential between two electrodes, it has been customary to adopt a convention about potentials:

Convention 7. **The potential of a standard hydrogen electrode is zero at all temperatures of interest.**

A standard hydrogen electrode consists of platinum black bathed with hydrogen gas at one atmosphere fugacity and immersed in a solution containing hydrogen ion in its standard state. The oxidation reaction at such an electrode can be written

$$\tfrac{1}{2} H_2(g) \rightarrow H^+(aq) + e^-(Pt) \qquad (31)$$

where $e^-(Pt)$ indicates an electron in the highest energy level normally occupied in platinum metal. Combination of equation (30) with convention 7 is equivalent to assigning zero values to ΔH°, ΔF°, and ΔS° for reaction (31).

Suggested Revision of Conventions

The requirements are now apparent for conventions that will permit the assignment of thermodynamic properties to individual aqueous ionic species such that equation (3) is satisfied, that will assign properties to the electron that satisfy equation (2), and that will satisfy the electrochemical convention 7. Conventions that satisfy these requirements most simply and that retain the most of former conventions seem to be:

Convention 5b. **Aqueous hydrogen ion in its standard state at any temperature has zero values for the quantities ΔH_f° and ΔF_f°; the value of S° at this temperature is equal to half the molar entropy of hydrogen gas at one atmosphere fugacity and the same temperature.**

Convention 6c. **An electron in the state $e^-(Pt)$ has zero values for the quantities ΔH_f°, ΔF_f°, and S°.**

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If these conventions are adopted, entropies tabulated at 25° for all positive ions of charge $+z$ will be $15.606z$ cal/mole deg more positive than formerly, and entropies of all negative ions of charge $-z$ will be $15.606z$ cal/mole deg more negative than formerly. Entropies calculated according to these conventions are included in Table 4.

Table 4. Entropy and Heat Capacity Values of Some Aqueous Ions at 25°C Based on Proposed Conventions[a]

Substance	State	$S°$ cal/mole deg	$C_p°$ cal/mole deg
H^+	aq	15.606	3.446
OH^-	aq	−18.125	−35.4
Cl^-	aq	− 2.44	−33.4
ClO_3^-	aq	23.4	−21.
ClO_4^-	aq	27.9	...
Na^+	aq	30.0	8.8

[a] These entries replace those for the same properties in Table 3. Values for $\Delta H_f°$ and $\Delta F_f°$ from that table should continue to be used. These entries are based on conventions 1–3, 5*b*, and 8*b* and are applicable with thermodynamic consistency to reactions of types A, E, F, and G, provided that for reactions of type F the electron is in state $e^-(0)$ if convention 6*a* is used and is in state $e^-(Pt)$ if convention 6*c* is used. Applications to reactions of types F and G do not give "correct" values for changes in thermodynamic properties.

Since entropies of positive and negative ions are changed in opposite directions by this change of conventions, reactions of types A and E would give the same changes in thermodynamic properties whether entropies from Table 3 or from Table 4 were used to make the calculations. Application to reactions of type F would be self-consistent, provided the state of the electron were assumed to be $e^-(Pt)$, and $\Delta S°$ in equation (23) would become 17.8 cal/mole deg as necessary for consistency. Application to reactions of type G would also be self-consistent, and $\Delta S°$ in equation (28) would become −5.3 cal/mole deg. For application to reactions of type F with electron state $e^-(0)$, convention 6*a* would have to be substituted for convention 6*c*.

These proposed changes in convention are not new. Klotz[4] has made an almost identical proposal. Van Rysselberghe[5] has also proposed such a change in the entropy assigned to aqueous hydrogen ion.

Estimation of "Correct" Thermodynamic Changes

Conventions 1–4, 5*b* and 6*c* form a set that also satisfies convention 7. If data for individual species are tabulated on the basis of these conventions, thermodynamic consistency (as defined by satisfaction of equation (11)) can be obtained by application of these data to reactions of types A, D, E, F, and G.

Reactions of types A, D, and E can be observed directly, and calculations from tabulated data are subject to experimental test. In addition to conventions 1–3, reactions of type D use only convention 4, and reactions of type E use only convention 5*b*. By the time balanced equations of these types have been written, the arbitrary assignments of thermodynamic properties have all cancelled out just as they do in discussions of potential energy changes in a gravitational field. Our confidence in thermodynamics assures us that any experimental test of such a reaction would confirm the predictions of calculations from these tabulations.

Reactions of types F and G are not subject to direct observation, although we can discuss them as hypothetical processes. They combine various chemical species in ways so that the arbitrary parts of the different conventions do not cancel out. Even though the conventions have been selected so that tabulated data can be applied with thermodynamic consistency to reactions of these types, calculated changes in thermodynamic properties will differ from the "correct" changes that we are convinced would be observed if the reactions could be carried out.

The problem can be illustrated with equation (25) as an example of a reaction of type G. This reaction can be written as the sum of three reactions

$$Na^+(g) + e^-(0) \rightarrow Na(c) \quad (32)$$

$$Na(c) + H^+(aq) \rightarrow Na^+(aq) + {}^1/_2H_2(g) \quad (33)$$

$${}^1/_2H_2(g) \rightarrow H^+(aq) + e^-(0) \quad (34)$$

Equation (32) can be treated with data from Table 2 and regarded as a reaction of type D if conventions 4 and 6*a* (instead of 6*c*) are applied to electronic states.

Equation (33) is half of equation (16) and is a typical reaction of type E giving the same value for calculations with data from Table 3 (convention 5*a*) or from Table 4 (convention 5*b*).

The conventions presented above assign zero values to changes in thermodynamic properties associated with equation (34). If the changes in these properties are not truly zero, the changes computed for equation (25) will not be "correct" even though they are self-consistent with regard to thermodynamic relations.

If it is desired to know "correct" changes in thermodynamic properties associated with reactions of type G, we must abandon convention 5*b* and determine the true changes associated with reaction (34). Because of the importance of this specific reaction, the subscript H will be used to designate properties associated with it.

An examination of experimental data on ionic hydration[6] has recently led to the following estimates:

$$\Delta H_H° = 99.17 \text{ kcal/mole} \quad (35)$$

$$\Delta F_H° = 104.81 \text{ kcal/mole} \quad (36)$$

$$\Delta S_H° = -18.9 \text{ cal/mole deg} \quad (37)$$

If these values are used with conventions 1–4 and 6*a*, thermodynamic properties of aqueous ions can be tabulated in such a way that they can be applied to give "correct" values for changes in thermodynamic properties during reaction of types F and G (provided reactions of type F assume the state $e^-(0)$ for the electron). These tabulated values will be as valid as the others for application to reactions of types A, D, and E. Table 5 presents such a tabulation. Note that conventions 5 and 7 have been discarded in the preparation of this table.

Although it might be desirable in principle to discard conventions 5 and 7 and to list properties of aqueous ions according to a convention that would give "correct" values for reactions of all these types, the practical difficulty arises that the numerical values in equations (35–37) are not known with the same precision as are

[4] Klotz, I. M., "Chemical Thermodynamics," Prentice-Hall, New York, 1950, p. 352.

[5] Van Rysselberghe, P., *Anales Real Soc. Espan. Fis. y Quim.*, 56B, 515 (1960).

[6] Noyes, R. M., *J. Am. Chem. Soc.*, 84, 513 (1962).

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thermodynamic properties of many electrolytes. Quantities like ΔF_H° are very subject to future modification and refinement, and any such modification would change all the values in Table 5. Until the changes in thermodynamic properties associated with reaction (34) are known with an accuracy at least comparable to the best data for formation of aqueous electrolytes from the elements, it is better to retain some form of convention 5 (and preferably convention 5*b* because of the consistency problems described above). Such retention requires the recognition that the conventions do not give "correct" values when applied to reactions of types F and G.

Table 5. "Correct" Thermodynamic Properties of Some Aqueous Ions at 25°C[a]

Substance	State	ΔH_f° kcal/mole	ΔF_f° kcal/mole	S° cal/mole deg
H^+	*aq*	99.17	104.81	− 3.3
OH^-	*aq*	−154.13	−142.41	0.8
Cl^-	*aq*	−139.19	−136.16	16.5
ClO_3^-	*aq*	−122.67	−105.43	42.3
ClO_4^-	*aq*	−130.58	−107.38	46.8
Na^+	*aq*	41.89	42.22	11.1

[a] These entries are based on conventions 1–3 and 6*a* combined with equations (35) to (37). They specifically avoid use of conventions 5*a*, 5*b*, and 7. They are applicable to reactions of types A, E, F, and G and will give 'correct" values for all including types F and G.

Application to "Absolute" Electrode Potentials

Convention 7 effectively assigns changes in thermodynamic properties to reaction (31). This reaction differs from reaction (34) only in the state of the electron. As has been indicated above, the property changes associated with reaction (34) have now been estimated with moderate confidence. If we could also evaluate the changes in thermodynamic properties associated with the potentially observable reaction,

$$e^-(Pt) \rightarrow e^-(g) \qquad (38)$$

the results could be combined to estimate property changes for reaction (31). Such data could then be used to compute "absolute" potentials for individual electrodes.

The problem of "absolute" electrode potentials is similar to the one of "correct" property changes for reactions of types F and G. If the standard free energy change of reaction (31) were known with sufficient confidence so that equation (30) could be used to assign the standard hydrogen electrode a potential known to better than 10^{-4} v, convention 7 could be abandoned in favor of a tabulation of "absolute" oxidation potentials. Until such time (which looks very far in the future), it is better to continue the present convention 7 while recognizing that application of tabulated data to half-reactions (type F) will not give "correct" values for changes in thermodynamic properties.

Effects of Changing Temperature

The above discussion has been confined to applications at 25°C. The heat capacity at constant pressure is defined by the equation

$$C_p = \left(\frac{\partial H}{\partial T}\right)_p \qquad (39)$$

Let $\Delta H_f^\circ(T)$ for a substance be the enthalpy change associated with formation of the substance in its standard state at temperature T from elements in their standard states also at temperature T. Also, let $\Delta C_p^\circ{}_f$ be the change in standard state heat capacity associated with forming the substance from the elements. Then

$$\Delta H_f^\circ(T_2) = \Delta H_f^\circ(T_1) + \int_{T_1}^{T_2} \Delta C_p^\circ{}_f \, dT \qquad (40)$$

$$S^\circ(T_2) = S^\circ(T_1) + \int_{T_1}^{T_2} (C_p^\circ/T)dT \qquad (41)$$

$$\Delta S_f^\circ(T_2) = \Delta S_f^\circ(T_1) + \int_{T_1}^{T_2} (\Delta C_p^\circ{}_f/T)dT \qquad (42)$$

$$\Delta F_f^\circ(T_2) = \Delta F_f^\circ(T_1) - (T_2 - T_1)\Delta S_f^\circ(T_1) - \int_{T_1}^{T_2} \frac{T_2 - T}{T} \Delta C_p^\circ{}_f \, dT \qquad (43)$$

Since heat capacity is a property having an absolute magnitude, no additional convention is needed in order to use these equations for preparing a table like Table 1 for the properties ΔH_f°, ΔF_f°, and S° at any temperature other than 25°. It is only necessary that values of C_p° and $\Delta C_p^\circ{}_f$ be known as functions of temperature in the interval of interest. Reactions of type A can be treated appropriately.

Since the heat capacity of $e^-(g)$ is $(5/2)R$, the data can also be used without additional conventions to prepare a table like Table 2 for any other temperature and to treat reactions of type D.

If ionic reactions of type E are to be treated, an additional "bookkeeping" convention is necessary. The one presently adopted[1] is:

Convention 8a. **The partial molal heat capacity of aqueous hydrogen ion in its standard state is zero.**

Data based on this convention are presented in Table 3.

Convention 8*a* represents an unfortunate choice because it cannot be combined with some of the other conventions without violating basic equations of thermodynamics. The arguments are similar to those developed for the inconsistencies in applying convention 5*a*:

Convention 8*a* can be applied to reactions of type E without inconsistency. The data tabulated in Table 3 can be used satisfactorily to predict temperature effects on changes in thermodynamic properties associated with reactions of this type.

If the electron in state $e^-(Pt)$ is assigned a heat capacity of zero, conventions 7 and 8*a* are inconsistent. Convention 7 requires ΔH° for reaction (31) to remain zero as the temperature is changed, and convention 8*a* does not permit this. Attempts to discuss electrode potentials and properties of ions at temperatures other than 25° will result in various contradictions and inconsistencies. The discrepancy could be removed without violating convention 8*a* if the heat capacity of $e^-(Pt)$ were assigned a value equal to half that of hydrogen gas, which at 25°C would be 3.446 cal/mole deg. Such a solution is not very satisfactory.

If the electron in a half-reaction (type F) is assigned a heat capacity of zero, combination of convention 8*a* with ΔH_f° values based either on convention 5*a* or 5*b* will lead to predictions for such reactions that violate the basic equation

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$$\left(\frac{\partial \Delta H^\circ}{\partial T}\right)_P = \Delta C_p^\circ \quad (44)$$

Thermodynamic consistency can also be saved for reactions of type F by assigning the electron a molar heat capacity equal to half that of hydrogen gas.

The inconsistency is at least as bad for reactions of type G, and there does not seem to be any way to correct the situation while retaining convention 8*a*. Consider the reaction

$$H^+(g) \rightarrow H^+(aq) \quad (45)$$

When data from Tables 1 and 2 are employed in equation (40),

$$\left(\frac{\partial \Delta H_f^\circ}{\partial T}\right)_P = 4.9680 - 3.446 = 1.522 \text{ cal/mole deg for } H^+(g) \quad (46)$$

Either convention 5*a* or 5*b* requires that

$$\left(\frac{\partial \Delta H_f^\circ}{\partial T}\right)_P = 0 \text{ for } H^+(aq) \quad (47)$$

If these results are applied to equation (4), then for reaction (45) we obtain

$$\left(\frac{\partial \Delta H^\circ}{\partial T}\right)_P = -1.522 \text{ cal/mole deg} \quad (48)$$

However, the data from Tables 2 and 3 for the same reaction give

$$\Delta C_p^\circ = -4.9680 \text{ cal/mole deg} \quad (49)$$

Equation (44) is clearly violated.

The discrepancies can be avoided by rejecting convention 8*a* and adopting the following one:

Convention 8b. **The partial molal heat capacity of aqueous hydrogen ion in its standard state at any temperature is half the molar heat capacity of hydrogen gas in its standard state at the same temperature. The heat capacity of $e^-(Pt)$ is zero, and of course that of $e^-(O)$ is also.**

Ionic heat capacities based on convention 8*b* are presented in Table 4.

This convention permits convention 7 to be retained and also permits consistent application of tabulated data to reactions of types F and G. Of course convention 8*b* will not give "correct" values of ΔC_p° for reactions of types F and G. Although an estimate of $\Delta C_p^\circ{}_H$ for reaction (34) could be made by the same type of procedure used to estimate the changes in other properties for this reaction, no such calculations have been made. These calculations will be undertaken in the near future if the necessary heat capacity data can be made. Until $\Delta C_p^\circ{}_H$ has been estimated, persons using data like those in Table 4 must realize that they give thermodynamically consistent results at different temperatures but that they do not give "correct" values for reactions of types F and G.

Effects of Changing Pressure

Pressure is the property usually used in addition to temperature to define the state of a chemical system. Of course

$$\left(\frac{\partial F}{\partial P}\right)_T = V \quad (50)$$

$$\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P \quad (51)$$

If molar volumes and coefficients of thermal expansion are known for various chemical species, thermodynamic properties can be calculated for temperatures and fugacities other than one atmosphere. No conventions are necessary for application to reactions of types A and D or for determining values for the species listed in Tables 1 and 2.

Application to aqueous ions does require a "bookkeeping" convention in order to assign the separate contributions of positive and negative ions to the volumes and coefficients of expansion of electrolytes. If the partial molal volume of aqueous hydrogen ion were set equal to half the molar volume of hydrogen gas, all negative ions would have absurdly large negative partial molal volumes. The most satisfactory convention seems to be:

Convention 9. **The partial molal volume of aqueous hydrogen ion and its temperature and pressure derivatives are all zero.**

This convention permits the potential of a hydrogen electrode to change with pressure, but no difficulty is introduced by this fact. Convention 7 requires the potential of that electrode to be assigned the value zero when the fugacity of the hydrogen gas is one atmosphere, but change of the potential with pressure can be handled by standard equations.

Summary

Many of the basic conclusions of this paper are presented in Table 6. They can be summarized as follows:

Chemists are not usually concerned with reactions that change atomic nuclei (type B) or that discriminate significantly among isotopic species of the same element (type C). The conventions usually adopted specifically exclude the possibility of such reactions.

Table 6. Applicability of Conventions to Reactions Involving Aqueous Ions

Convention combinations[a]	Table of typical data	Reaction type E	Reaction type F[b]	Electrochemical convention 7	Reaction type G
Conventions 5a and 8a	3	Valid	Inconsistent for 6a and 6c; consistent for 6b	Inconsistent	Inconsistent
Conventions 5b and 8b	4	Valid	Consistent for 6a or 6c if electron state specified; inconsistent for 6b	Consistent for 6c; not applicable for 6a and 6b	Consistent
Thermodynamic data for reaction (34)	5	Valid	Correct for 6a; not applicable for 6b or 6c	Not applicable	Correct
Thermodynamic data for reactions (31) and (38)	5	Valid	Correct for 4; other conventions not applicable	Superceded by absolute electrode potentials	Correct

[a] All combinations assume conventions 1–3. The last one also assumes convention 4, as do all applications to reactions of type G.
[b] Application to reactions of type F requires specifying the state of the electron.

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If such reactions are excluded, it is permissible to make as many separate assignments of enthalpy and free energy as there are elements. These assignments are made by defining enthalpies of formation (convention 1) and free energies of formation (convention 2) that are zero by definition for each element in its standard state at any temperature. Entropies (convention 3) are based on assigning the same (zero) value to all perfect crystals at sufficiently low absolute temperature.

These conventions are sufficient for treatment of reactions that include no charged species other than aqueous ions provided the equations are electrically neutral (type A).

Extension to reactions of gaseous ions (type D) assigns no energy other than kinetic energy to a gaseous electron (convention 4).

Extension to non-neutral equations for reactions of aqueous ions (type E) customarily assigns zero values to ΔH_f°, ΔF_f°, and S° for aqueous hydrogen ion in its standard state (convention 5*a*). This convention is unfortunate because tabulated data for aqueous hydrogen ion and for all other aqueous ions fail to satisfy the equation

$$\Delta F_f^\circ = \Delta H_f^\circ - T\Delta S_f^\circ \qquad (3)$$

The inconsistency does not affect application of tabulated data to reactions in which the only charged species are aqueous ions (type E), but violations of basic thermodynamic equations result from attempted application to half-reactions (type F) and to transport of ions between gaseous and aqueous phases (type G).

If the partial molal entropy of aqueous hydrogen ion is set equal to half the molar entropy of hydrogen gas (convention 5*b*), the entropies of all positive ions at 25°C become more positive by $15.606z$ cal/mole deg, and entropies of all negative ions become less positive by the same amount. This change of convention does not affect changes in thermodynamic properties computed for reactions of type E but permits thermodynamic consistency for properties computed for ion transport reactions (type G). It also permits consistency for half-reactions (type F) if the electron is assigned a state $e^-(0)$ having zero values of ΔH_f°, ΔF_f°, and S° and also consistent with convention 4 (convention 6*a*).

Even though these conventions permit self-consistent application, they do not give "correct" values for changes in thermodynamic properties for reactions of types F and G. "Correct" values could be obtained if it were possible to determine changes in thermodynamic properties for the reaction

$$\tfrac{1}{2}H_2(g) \rightarrow H^+(aq) + e^-(0) \qquad (34)$$

Reasonable estimates of these quantities are possible, but the probable accuracy does not justify abandonment of convention 5*b* (although the argument of thermodynamic consistency does justify substituting convention 5*b* for the present convention 5*a*).

If zero values of ΔH_f°, ΔF_f°, and S° are assigned to an electron in the highest occupied energy level in platinum metal (convention 6*c*), the simultaneous application of convention 5*b* (but not of convention 5*a*) is consistent with the electrochemical convention that the potential of a standard hydrogen electrode is zero at all temperatures of interest (convention 7). The evaluation of the "absolute" potential of this electrode would require knowledge of changes in thermodynamic properties associated with reaction (34) and also with the reaction

$$e^-(Pt) \rightarrow e^-(g) \qquad (38)$$

The partial molal heat capacity of aqueous hydrogen ion is usually assigned the value zero (convention 8*a*). Such an assignment is satisfactory for reactions of type E, but it is not consistent with the electrochemical convention (convention 7). Application to reactions of types F and G leads to violation of the equation

$$\left(\frac{\partial \Delta H^\circ}{\partial T}\right)_P = \Delta C_p^\circ \qquad (44)$$

These inconsistencies can be eliminated by assigning aqueous hydrogen ion a partial molal heat capacity equal to half the molar heat capacity of hydrogen gas in its standard state (convention 8*b*). This convention permits thermodynamically consistent but not "correct" calculations of temperature dependence of reactions of types F and G.

Apparently no difficulties arise in the treatment of pressure changes if zero values are assigned to the partial molal volume of aqueous hydrogen ion and to the temperature and pressure derivatives of this quantity (convention 9). If this convention is adopted, the assigned potential of a hydrogen electrode becomes a calculable function of the fugacity of the hydrogen gas.

Because of the inconsistencies with the electrochemical convention (convention 7) and during applications to reactions of types F and G, it is strongly recommended that the presently accepted conventions 5*a* and 8*a* be replaced by conventions 5*b* and 8*b*.

Acknowledgments

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Professor Henry S. Frank of the University of Pittsburgh provided helpful discussion at the time I discovered the inconsistencies in application of existing conventions to ion transport reactions (type G). Professor Pierre Van Rysselberghe of Stanford University called a reference to my attention, and Professor T. F. Young of the University of Chicago encouraged me when I suggested the desirability of a discussion of these conventions. Professor John A. Schellman of the University of Oregon and Professor Irving M. Klotz of Northwestern University read the manuscript and made helpful suggestions.

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Programed Instruction

Introduction

Although its proponents claim so, it is by no means clear to teachers of chemistry that programed instruction is a remarkable teaching technique. At this symposium an invited group of high school teachers and college professors who have had personal experience in the use of programed instruction discuss their views.

Briefly stated, the speakers are convinced, strongly so, that programed instruction is a useful teaching tool. We all hope to convince each interested teacher that programed instruction in chemistry is at least of sufficient value to warrant his detailed, thoughtful, examination. Optimistically, we hope that such an examination, which cannot be completed in one symposium, will convince readers that this new version of a very old idea, first used (or first recorded as being used) by Socrates, is indeed all that will be claimed in the discussions which follow.

It must be emphasized that further study and diligent, time-consuming effort is required to reach an informed decision, pro or con. The references cited by some of the speakers will provide important literature on the subject.

The symposium is divided into three more or less non-overlapping parts. The first papers discuss what programed instruction is, the criteria of evaluation, and the underlying reasons why programs are worth careful attention. The remaining papers describe what has been done at the author's institution, a "how-we-did-it" exposition.

In most symposiums, a few speakers discuss selected topics for about one hour each, or longer. The complexity of this symposium topic warrants discussions of this length; but the topic is new, and since those of us who think programed instruction is valuable enough to demand attention represent a wide spectrum of experience and opinion (some quite contradictory), it seemed desirable to invite more speakers, with a consequent cutting down of the time available to each.

J. A. Young, *Symposium Chairman*
King's College, Wilkes-Barre, Pennsylvania

Jay A. Young
King's College
Wilkes-Barre, Pennsylvania

Both Can Benefit, Student and Teacher

Programed instruction is only one more tool for the teacher. It is not the answer to all our teaching problems. However, the effectiveness of programed instruction as a teaching tool is enhanced by a second, outstanding characteristic—its utility as a device for the self-improvement of the teacher who prepares a few programs of his own.

This theme, *programed instruction is useful to the teacher as a means of self improvement*, can perhaps best be demonstrated by mentioning two key words, followed by an elaboration of their application within this context. The words are control and order.

Most teachers agree that, if learning is to occur, a rather rigid, though friendly, control of the student is necessary. A major problem has been to exercise this control. By what might be called a psychological subterfuge, programed instruction can control the student, at least to a remarkable degree.

However, control by itself is insufficient. The knowledge to be imparted must be presented in an order which is communicable to the student. This, really, is the point. By the use of programs which the teacher himself has prepared for his own students, the teacher learns how to present information in an orderly manner which is communicable to the student.

To illustrate this, refer to Figure 1, which is a portion of a program intended to help students comprehend

Presented at the Symposium on Programed Instruction at the 124th meeting of the American Chemical Society, Atlantic City, New Jersey, September, 1962.

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the concept of concentration. This type of programed instruction is a linear program.

A linear program consists of a series of brief (usually) expository statements, in which the student is subtly interrogated as he procedes, i.e., he fills in the blanks. The student is led in a direct linear manner from the initial to the concluding statement. An intrinsic program, as is described in detail in a following paper in this symposium, consists of a series of pairs of exposition-question sets. Each of the several direct questions which is used in such a program is intrinsic with the exposition which precedes the question.[1]

Both types have their particular areas of use and their vigorous proponents. Both linear and intrinsic techniques can be used; many of the best recently produced programs include both features, although one or the other will predominate. To clarify the discussion, however, the example used here will illustrate only the linear technique.

Paragraph, or "frame," number 43 is read by the student, and the single missing word is supplied by him. While reading the frame, the student covers the answer printed in the margin. After supplying what he thinks is the correct word, the answer is uncovered; and the student learns whether he is, or is not, correct. The student procedes in a similar manner with each of the following frames.

If the student cannot think of a word or words to fill the blank, he may look at the answer in the margin and then proceed. Because students are not, in a properly prepared program, challenged beyond their ability—though they may indeed be challenged, they do not tend to look at the answer in the margin without first attempting to determine their own answers. Students quickly recognize that they are only cheating themselves when they look at the answer without first attempting to determine their own answers. Since no grade is ever given for a good or a poor answer, there is little temptation to use the program incorrectly.

Whenever the student cannot supply the word or synonyms to the word printed as the correct answer, the author of the program has failed because he was not thinking along the same lines as the student. A program is, quite literally, a test in which the student supplies answers. But if the student supplies an answer which differs from that of the author of the program, it is the author who is wrong, not the student. This student is no longer under the control of the program writer.

Typically when this occurs, the author has, in some prior frame or two, failed to set the stage so that what he had to say in the following frames was communicable to the student. Sooner or later, the student will run off the track of the argument and fail to learn. All of us have had this experience while studying from a text or reference work. When studying material which is difficult to comprehend, we think as we study; and, agreeing with the logic of the textbook author's statements, we proceed sentence by sentence. Then, abruptly, we discover that—in the middle of a paragraph—we can no longer identify our agreement with the author's statements. Somehow, perhaps in the preceding sentence, perhaps in a sentence three pages back, we got the wrong impression, and this now arises to render communication difficult.

In such a case, of course, the scholarly student will back up and re-read the preceding pages until he finally identifies his misunderstanding. Then, with this clarified, with communication once more well established, he proceeds with his study.

With few exceptions, this is not the way college freshman students study their text. Although the text may indeed be one of the best available, there will be places in it where the student fails to understand what the author meant for him to understand. Since the beginning student does not recognize this, he will not always know what to do in order to clarify the matter.

Figure 1 supplies a specific illustration of the means by which programed instruction avoids this difficulty. Refer, for example, to frame number 48. Suppose that you have volunteered to study this program, which I have just written a few hours ago, to help me find the places where I have failed to communicate. You have gone through the first forty-seven frames easily, but you cannot, from what you have learned thus far, even with diligent reflection, think of a word (or number) which will fill the blank in frame 48. Or, you have thought of a word but on checking the marginal answer find that we disagree. As the author of the program I have failed to communicate.

It is up to me, by discussing the matter with you in an informal way, or by judging from the word you did supply, to determine where I failed to communicate with you. Suppose that I determine that I gave you the wrong impression back in frame 27. Before I give this program to another volunteer, I will revise the program beginning with frame 27, and also revise frames 28, 29, and so on, as I think necessary, until the error I have made is presumed to be corrected. Then, if the second volunteer now gets by frame 48 without incident, I have communicated, at least for volunteer number two.

By trying out the original version on a few students, noting where I made mistakes, and what kind of wrong words the student wrote in those frames, by revising the program to remove these difficulties, and finally by giving the students an examination I learn that for these students I have written a program which will teach because it does communicate.

The major point is what happened to the teacher who wrote the program. That teacher had a unique experi-

[1] See following papers in This Symposium, THIS JOURNAL, 40, 14-28 (1963).

The cover



The busy professor (note the stack of papers!) is also puzzled. On the desk of Mr. Gordon E. Highriter of King's College are spread out all the programs currently in print for teaching chemistry. Also available is the standard reference book in the field, Lumsdaine and Glaser. Photograph by Ace Hoffman Studios—Wilkes-Barre, Pennsylvania.

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ence! He found that some of his favorite explanations were not understood and that some of his previous students have learned in spite of what he did. But more than this, he now knows precisely where he erred in his presentation. He has tried, by the successive revisions, to express himself to the students in a new and better way. If he persisted in his efforts, he now knows how to explain concepts in this one area more clearly to his future students. This knowledge makes the effort worth while.

But even more remarkable and pleasing is a further bonus. All who have prepared programs in the manner outlined here have discovered that there is a mode of expression, an order of presentation, an effective control of the student as he thinks, which is communicable to the student in other situations. To put it differently, every teacher who tries diligently to prepare a few successful programs for his own students finds that he has learned how to express ideas in an understandable manner to his students in all of his contacts. I cannot put this too strongly: if you would like to learn to improve your ability to teach students, then write a few programs in the manner described. You will be both amazed and pleased with the results.

In actual practice you need not revise your programs so finely that every student correctly answers every frame. There are some subtle arguments which indicate that it is desirable at times to allow the student to answer incorrectly, provided that this is anticipated and corrective steps have been taken in following frames.

The proper preparation of programs is time-consuming. Many of the speakers at this symposium have prepared programs for their own students and some of them are now, or soon will be, available from publishers. However, no teacher will profit as much as he should, or could, using only programs prepared by another.

No teacher should attempt to prepare programs for his students armed only with what he learns from this symposium. A list of useful references for the beginner is included in the footnote.[2]

Some have heard that programed instruction is good for rote material, such as the learning of oxidation numbers or symbols of the elements, but that it is not well-suited for other purposes. My experience has shown that programed instruction can best be used to teach principles and comprehension of ideas, and that it is not well-suited for the mere presentation of information to be memorized. Dr. Benfey will elaborate upon these remarks in his discussion.

I have purposely avoided mentioning mechanical devices called "teaching machines." At least at the upper high school and freshman college levels, mechanical devices are not essential for most applications. They are not harmful, but they are cumbersome.

Programs present information in very small steps. At first inspection a sample program may appear to be too simple. Do not be misled; unless a program does indeed offend by its simplicity and the care which it takes to spell out details which are quite obvious to any competent teacher, it is likely to be a poor program.

Because of this apparent simplicity, it might also seem that students who use programs will tend to lean on them as though they were a crutch, and will become less able to use ordinary text material. I have found the contrary to be true. When programs are used as adjuncts to a good text in elementary chemistry, the students tend to be weaned away from the programed instructions rather quickly. They learn from the examples set by the programs how to extract information from a text for themselves. One might say that, at last, they have learned how to read intelligently, while asking questions of the author and providing their own answers.

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[2] See DAY, J. H., J. CHEM. EDUC., **39**, 50 (1962); **36**, 591 (1959) and the Literature Cited therein; YOUNG, J. A., J. CHEM. EDUC., **38**, 463 (1961); and LUMSDAINE, A. A., AND GLASER, R., editors, "Teaching Machines and Programmed Learning," Department of Audio-Visual Instruction, National Education Association, Washington, D. C., 1960, especially pp. 401–5, 486–96; STOLUROW, L. M., "Teaching by Machine," U. S. Office of Education, HEW, Supt. of Documents, Washington 25, D. C., 1961; RIGNEY, J. W., AND FRY, E. B., *Audio-Visual Communication Review*, 9, no. 3, 1961.

43. It is not enough to know what we know now, the way to calculate concentrations. We must also be able to make solutions, in the laboratory, that have a known concentration. For example, a chemist wished to prepare 250 ml of a 0.12 molar solution of potassium bromide. (Since this is an ionic compound, some chemists would say that the concentration of this solution would be 0.12 _____.)	formal, or, F
44. How would this solution be prepared? First, we know that a certain quantity, which we shall have to calculate, of potassium bromide should be weighed on a balance. Then this weighed quantity will be dissolved in a suitable amount of water, and, with thorough stirring, more water added until the total volume of the solution is _____ ml. The question is, of course, how many grams of potassium bromide do we need?	250
45. The desired concentration is 0.12 molar. Writing this as a fraction, with a 1.00 in the denominator, we have _____.	$\frac{0.12 \text{ mole of KBr}}{1.00 \text{ l}}$
46. But we want only _____ ml of solution.	250
47. Or, expressed in liters, we want _____ l of solution.	0.250
48. Therefore, if we multiply the numerator and the denominator of the fraction, in frame 45, by _____, we will have the proper volume, 0.250 l, in the denominator and the number of moles in the numerator will be the correct number of moles of potassium bromide for our 250 ml of solution.	0.250
49. Carrying out this multiplication, we have, for our new fraction: _____.	$\frac{0.030 \text{ mole of KBr}}{0.250 \text{ l}}$
50. So, we need to weigh out _____ mole of potassium bromide (or correctly, we need to weigh out _____ g formula weight, since potassium bromide is an ionic compound) for our solution.	0.030 0.030

Figure 1. Eight consecutive frames selected from a program on the concept of concentration.

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Intrinsic Programs

One perfect way to learn would be to read a textbook that was clearly written, so logical and complete, that one could not fail to understand. This textbook has unfortunately not yet been written. In simple fact, *most* people cannot do a very good job of learning from *most* books. The reasons are numerous but fairly simple: first, each text assumes that a certain background is possessed by the reader, but without specifying that background in other than a general way. For example, a problem on the osmotic pressure of blood that does not specify the solvent just might frustrate a student with no biology background.

Another trouble is that books are generally written for the teacher, not for the student, and the teacher must fill in the missing pieces for the student. But if a single point is left out or slurred over, the beginning student may well be lost, so that the whole topic is a source of confusion. Most books are guilty to some degree.

There are other troubles. The student does not always read well and accurately, and sometimes he only skims. He is usually unable to separate the major ideas from the incidental description, and he almost never stops to work out each idea as it appears and make it his own.

If only the student could be kept on one idea at a time until he mastered it, then half-mastery would not plague his further progress. If only the interested, working student could ask the crucial question at the precise time he needs the answer, and if only the student could know whether he is on the right track as he goes, most of these defects would disappear.

Programed instruction is the one approach to learning that makes an honest and total effort to correct all the troubles mentioned above. It is first judged successful in terms of student success, not in terms of teacher evaluation. It forces the student to learn every single point, one at a time, and to make it his own property through his own activity. It can correct him when he gets off the track, and reassure him at every step he takes that is right. When the student has gone through a well-written program, there is no need to ask whether he has learned or understood the material.

Unfortunately, programs have their drawbacks too. They can easily become boring or tedious or both. They are prodigal of space, time and paper.

But they can have two very greatly beneficial effects. The first, and maybe even the most important, is in teacher improvement. The teacher who conscientiously writes a program—no matter what kind or how small—on a topic that gives the students trouble will find possibly to his bewilderment and certainly to his enlightenment, just exactly how much prior knowledge is expected of the student. He will also find that the small, simple concept he started out to explain is fraught with perilous assumptions which we have long since learned to swallow, that are very hard indeed to swallow the first time. The experience then of revising, based on student error and difficulty, adds a chastening sense of modesty to the teacher's confidence in his ability to explain. And at the end, the teacher has learned a new appreciation, not only of his subject, but of the importance of his own task. He cannot fail to be a better teacher for the experience. Dr. Young has stressed this in his remarks.[1]

The second beneficial effect of programed instruction is its great usefulness for the student. Probably in chemistry the best place for programs is as small individual units, designed to teach a single concept. They can be, and should be, used together with every other resource the teacher has—lectures, tutoring, TV, movies, film strips, demonstrations, laboratory, homework, and if possible, discussion. Programs may best be used to carry the small fortresses of difficulty that are perennial holdouts; how to solve weight-balance problems, how to balance redox equations, and so on. The programs can be used either to introduce the subject, or to supplement or replace the textbook on that subject.

The validity and success of programs have now been well established, especially in the armed services, and in the whole world of industry, including such management functions as decision making.

The Intrinsic Program

The intrinsic program differs substantially from the linear program.[1] The figures taken from an intrinsic program dealing with the kinetic molecular theory will illustrate this. Notice that first the target population is defined (Figure 1). Anyone who has finished at least part of a course in high school chemistry and physics should have no trouble; we are aiming primarily at the college freshman and the physical chemistry student.

The objectives of the program (Figure 2) are carefully spelled out, so the student knows what it is he will be able to do when he has finished. Notice also that the background knowledge required is completely and exactly specified, so the reader will know whether he is ready for the program or not. In all three instances programed instruction is sharply distinguished from the textbook and other forms of learning materials.

Presented at the Symposium on Programed Instruction at the 124th Meeting of the American Chemical Society, Atlantic City, New Jersey, September, 1962.

[1] See Preceding paper in This Symposium, THIS JOURNAL, 40, 11 (1963).

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IS THIS PROGRAM FOR YOU?

This program is designed for the reader who has completed at least a high school course in Chemistry or Physics. It will be most useful to students in General Chemistry and in Physical Chemistry.

Figure 1.

PREREQUISITES

It is assumed that you know or are familiar with the following:

1. That a molecule is the smallest particle of a compound; for example, that O_2 is a molecule of oxygen.
2. That all molecules of a pure substance are identical (ignoring isotopes for now).
3. That an "atmosphere" is a unit of pressure, sufficient to support a column of mercury 760 mm in height. This is about 14.7 lb/in.^{2}.
4. That a "liter" is a unit of volume. It is a little larger than a quart.
5. That the equation for a straight line has the form

$$y = ax + b$$

where a and b are constants.

Figure 2.

Your answer was, "Exactly 25 lb/in.^{2}." You are correct.

If the container is not distorted or the temperature changed, the pressure will remain constant forever if the container is absolutely air-tight.

But the molecules hit the wall, and certainly they must collide with each other frequently. If we know the pressure remains constant over time in a sealed container, and if we know the moving molecules are hitting the wall and colliding with each other, what can you conclude about what happens as a result of these collisions?

Page 17 (1) that of two molecules colliding, together they have exactly as much kinetic energy as before.

Page 18 (2) everybody knows that when two objects meet there is friction, so the colliding molecules will have less energy after colliding than before.

Page 19 (3) since some collisions will be head-on and some sideswipes, then some molecules will get going faster than others.

Page 20 (4) if the molecules are not round, (for example, acetone molecules) then some energy may go just to spinning the molecules around.

Figure 3.

page 18

Your answer was, "Everybody knows that when two objects meet there is friction, so the colliding molecules will have less energy after colliding than before."

Follow the line of reasoning to its conclusion and see where it ends. If energy is lost on collision, then after a while there would be no energy left. And no energy of movement means no pressure would be exerted. No pressure is zero pressure—and this is a *perfect vacuum*!

It just does not happen. But it would happen if *any* energy were lost on collision. Since this does *not* happen, then *no* energy is lost on collision. In other words, the molecules are 100% elastic!

Now turn to page 17.

Figure 4.

page 20

Your answer was, "If the molecules are not round, then some energy may go just to spinning the molecule around." You are correct.

It is possible for two molecules to collide dead center, but since collisions will be at random, most will strike *not* in the center.

An off-center hit will spin the molecule; just as when you throw a baseball bat, the bat *spins* and flies through the air simultaneously. So, with molecules which are not spherically symmetrical, some of the kinetic energy is rotational as well as translational. It is still kinetic energy, and may be passed on in the next collision as a new distribution of rotation and translation, just depending on what *part* of one molecule hits what part of the other molecule.

To see how this works, put a pencil on the table and strike it near the end. Notice that the pencil *turns* as it moves.

Turn to page 17.

Figure 5.

At the end of the program there is a short objective test, so the student can find whether he has mastered the material in the program or not. If there is an error or uncertainty, the correct answers given on the next page also direct him to the page in the program where the point is discussed for whatever review or clarification is necessary.

Again, this attitude is unique to programs; the reader at the end knows exactly how well he has mastered the material; and if there is something missed, he knows exactly where to go to remedy the defect.

Now consider a few frames from near the end of Part I of the Kinetic Theory of Gases which my students have used for the past few years (see Figures 3, 4, and 5). First, the question is repeated, and confirmation of correctness given, then confirmation of the reasoning that must have been involved (or at least the reasoning that would correctly lead to this page). Then a further question is asked about one detailed aspect of the picture the reader has by now drawn. He is steered to think about a question that will be fruitful.

Notice that of the four answers presented for choice, three are correct, and the fourth is certainly reasonable and not so novel or shocking that it will be remembered. To see what happens if the one wrong choice is made, note Figure 4.

If the student chooses page 20, he will be confronted with Figure 5. Then he is led to look at the other correct answers. In other words, he sees all the three correct answers, but has chosen the order in which he will see them. The correct answers eventually all lead to the next subject, and so on.

The concept presented on a single frame is not necessarily a single nor a simple concept, but it is a unit, a single piece, which the student must absorb before proceeding.

The objection that it is bad pedagogy to suggest wrong answers does not necessarily have great validity if all possible choices are presented with real purpose. In any event, the multiple choice test question is here to stay, and students are familiar with them. Students are test-wise and not easily led astray by even a formidable array of wild choices, no matter how novel or interesting.

The intrinsic program has the advantages of providing various sized steps and correction for errors; it is

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less boring, and probably more acceptable to the better students, while less well adapted to the poorer.

Programs are appearing on the market, and every teacher must not only decide whether he will use them, but also learn how to recognize and separate the good ones from the bad. I also concur heartily with the opinions already expressed that a sure way to become a better teacher is to try conscientiously to write a program.

General References

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Center for Programed Instruction
New York, New York

Evaluating a Chemistry Program

How should one evaluate a chemistry program? Unfortunately, it is not possible to evaluate a program simply by examining its contents the way one appraises a new textbook. The effectiveness of programed instruction is determined by the way students respond to working with it. Whereas textbooks are all too often written for teachers rather than students, programs are written strictly for students. However, there are certain criteria one can apply in making a preliminary judgment.

Just as a textbook cannot contain inaccuracies, a program which makes misleading statements is also unacceptable. I do not refer here to obvious misstatements, since it goes without saying that they are as unwarranted in a program as in a textbook. What I am referring to is a fault unique to programed instruction. One reason for its occurrence is a prevalent misconception that the exigencies of programing technique justify extreme oversimplification. Because of its incompleteness, this excessive oversimplification can be as misleading to students as an actual misstatement.

For example, a program which was written for high school students introduces atomic structure in the following way: A pile of pebbles is described as being as physically reduced to sand and then to powder. The observation that individual powder particles are extremely tiny is followed by the statement that each minute powder particle is made up of even tinier particles called atoms. Each of the statements by itself is acceptable enough. However, their total implication is that atoms can be obtained by a process of physical subdivision analogous to reducing pebbles to powder.

The inference of incorrect ideas from what is left unsaid is a fault which is specific to programs and therefore difficult to detect at first glance.

Another reason for the frequent occurrence of this defect is the very characteristic of programed instruction which is chiefly responsible for its impressive effectiveness. This is the focusing of attention on the significant material to be learned. To get the point across it is expedient to be as direct as possible. Therefore, the tendency is to include only the bare minimum of information. This is not always a good idea, particularly with the subject matter of science, since the concepts being taught are seldom black and white. Some degree of qualification is usually necessary to develop the proper perspective.

For instance, in another program written for high school students, the definition of a chemical compound is developed from the law of constant composition. It is implied quite unintentionally, since it is never actually stated anywhere in the program, that the composition of *all* chemical compounds is invariable. Since bertholide compounds are usually not mentioned in high school, they cannot be discussed in this program. Therefore some other qualifying statement is necessary to the effect that compounds with variable composition *do* exist. If there is no qualifying statement to the contrary, a programed sequence which concludes that all A is B will also imply its converse. Such an implication is frequently incorrect. In evaluating a chemistry program it is especially important not only to look for sins of commission but also to look for sins of omission which can be equally deceptive to the student.

Unique Properties of Programed Instruction

There are three properties which uniquely characterize programed instruction. The first is the logical and systematic presentation of the subject matter. This hierarchical arrangement of the material to be learned makes the mastery of fundamental concepts much more likely. The analysis of the subject matter which has to be accomplished to program it successfully is far more rigorous than is generally made for textbooks or lectures. For example, the three laws of chemical change are usually taught *seriatim*, immediately preceding the discussion of Dalton's atomic theory. Students seem to have the most difficulty understanding the law of multiple proportions and I found out why when I tried to program it that way. Historians tell us that Dalton predicted this law as a *consequence* of his atomic theory. When taught in *this* sequence it makes much more sense. In the program, the student actually follows the reasoning Dalton used when he made his prediction. It

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becomes both an interesting exercise in deductive reasoning and a much clearer explanation than is usually presented.

The second characteristic property of programed instruction is that the student's attention is continually directed to what he is supposed to be learning. This focusing of attention on the significant material is at present largely achieved through the responses the student is required to make.

We can illustrate by referring to Figure 1. These frames are at the beginning of a program for high school students on the kinetic-molecular theory of gases. This first part of the program explains what a mental model is and why it is useful to scientists. Examining frames out of context is especially difficult. Therefore I would like to point out that even though the answers required

Response	*Question*
	8. When a small bottle of a strong-smelling gas, for instance ammonia, is opened in one corner of a large room, eventually we can _____ it all over the room.
Smell	
	9. It appears that the molecules of the gaseous ammonia must have_____ _____fairly quickly throughout the room.
Spread, traveled, moved, etc.	
	10. To explain this ability of gases to spread out rapidly in all directions, scientists imagine that the molecules of a gas must be constantly (your best guess) (_____ _____).
Moving, in motion, etc.	

Figure 1.

may seem at first inspection to be obvious, they are demanded by the need to set carefully the initial stage for the idea being developed, namely that molecules of a gas are always on the move. There are two more frames in this sequence followed by a programed black box experiment.

The third unique property of programed instruction is that the student plays an essential part in its construction. At every stage in the development of a program the student is the judge of its effectiveness.

I have not mentioned "immediate confirmation of response," a phrase frequently used in describing programed instruction. An experiment recently performed by the Educational Testing Service in Princeton indicates that this is not quite as essential as previously thought. Briefly, a group of bright tenth grade students worked through the first 250 frames of my program on the gas laws, in which all the answers were omitted. These students not only kept going even though they never had any sure way of knowing whether they were correct, but they did remarkably well on an examination written by ETS. The part that really has given us pause is that they performed as well or better than a group of equally bright students who had all the answers!

What I have been trying to present in this discussion is an operational definition of programed instruction. The discrimination between a program and a non-program is made in terms of what it *does* rather than what it *is*. Consequently, appearance alone is not a sufficient criterion for judging a program. We can expect to see programs in the future which bear little or no superficial resemblance to our current Model-T versions.

Is it possible to decide just on the basis of the style of presentation that one program will necessarily be better than another? My own investigations in developing programed instruction in chemistry during the past two years have led me to combine both the linear and branching intrinsic techniques, to call for both constructed and multiple-choice responses, and to include frames containing only one sentence and frames several paragraphs long. There are places where the student reads without making any responses and other places where he is asked to respond to a question like the following: "Explain why there cannot be a temperature below absolute zero." (This question is the terminal frame in a sequence discussing temperature and kinetic energy.)

There also seems to be a general impression that some optimal length is required for individual frames. On the contrary, frames should be as long or as brief as is necessary for both clarity and completeness. In fact, within a given program unit it is a good idea to vary both the length of the frames and the kinds of responses called for. This makes for more interesting programing but, even more important, it affords maximum flexibility in the presentation of the material.

Students work as long as an hour at a time on a program and in general concentrate much harder than when studying from a textbook. Therefore programs should be written in the same kind of lucid, expository prose found in the very best textbooks with a generous sprinkling of clearly drawn illustrations and diagrams. All other things being equal, a well-written program will hold the student's interest longer and consequently will be more effective. However, there is nothing inherent in a particular programing technique that makes it more interesting or a better teaching tool.

Since no program can be expected to teach everyone, it is necessary to know the student population for whom it is intended. This information can either be the particular prerequisite knowledge presumed in the program or a description of the minimum ability level needed to learn from it. Also, a program should be accompanied by a statement of its objectives: what the author claims it teaches.[1]

One final criterion for chemistry programs is that they should be maximally self-instructional. Students should be able to learn from them with a minimum of supervision. By working on programs for homework instead of the usual less productive assignments, students could probably learn most of the basic concepts in chemistry on their own. This would make available for other purposes the class time usually spent in teaching these fundamentals.

The value of programed instruction in teaching chemistry has impressed almost everyone who has given it a try. By refusing to accept chemistry programs which do not at least meet these minimum criteria we can discourage damaging exploitation which could prevent this remarkable new teaching technique from being developed to its fullest potential.

[1] See previous papers in This Symposium, THIS JOURNAL, 40, 11 (1963).

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Programing as an Aid to Effective Chemistry Teaching

The "teaching machine" is of course nothing new—we have seen it in the form of flash cards for language instruction and in the toys of our childhood which light up when the contact device touches the correct button. These were devices that someone marketed and the teacher in school and college used them if he liked them. No evidence went with them claiming to prove that they aided the teaching process.

What is relatively new about self-instruction devices —of which the ordinary hard cover book is still and is likely to continue to be by far the most prevalent—is the application of approaches characteristic of scientists to the development, modification and evaluation of such devices. Statistical analysis is available with all its power and pitfalls to give an indication whether learning has in fact improved. In addition the subjective responses of students and teachers can be elicited to help determine whether learning by means of self-instructional devices has been more efficient, enjoyable, and effective. Early enthusiasm cannot, however, be taken as proof of success, particularly if the students know that they are guinea pigs in an experiment.

Earlham College has experimented with self-instruction devices from tape-recorders used to improve foreign language pronunciation, to "Skinner machines" and mimeographed materials in a dozen or so liberal arts fields. The work was supported in part by a grant from the Department of Health, Education and Welfare[1] and was organized under a director conversant with developments in the subject and with research in the psychology of the learning process.

The chemistry department was intrigued with the possibility of (1) developing instructional materials on particular topics which an instructor may safely assume is known by a large majority of the class but which some students may not have mastered in high school (or earlier college courses). Examples are the use of exponents and logarithms, the writing and interpretation of molecular formulas, and the balancing of simple chemical equations. With these programs students who have had inadequate or no previous high school instruction in the subject can bring themselves up to the level of those who have. Students familiar with the material can discover a new approach to it and may learn a clear, logical development of the ideas on which a solid college course can then be built. Such materials might also be useable on the high school level.

We also wished (2) to simplify instruction in topics that might be called the scaffolding of chemistry—topics not very significant in themselves, but needed in order to simplify the later discussion of chemical systems. Examples are the writing of Lewis structures (electronic formulas), ionic and oxidation-reduction equations, the computation of "formal charges," the unambiguous naming of organic compounds and the writing of isomeric structural formulas. The proper procedures for carrying out such assignments require very careful following of directions in a stepwise fashion. Such directions are usually only imperfectly learned through lecture presentations, textbook assignments, or problem sets. It was thought that programed instruction in these topics might be able to transmit the proper steps in a way which would assure mastery of the simpler stages before more complicated problems are attempted.

We were also interested in seeing (3) whether programed instruction is as useful in advanced chemical discussions as it seems to be in the beginning stages. We have prepared a program for calculations based on volumetric analyses and one dealing with colligative properties of solutions.

A fourth goal, (4) the exploration of the use of pre-laboratory, laboratory, and post-laboratory instruction, has us most puzzled at the moment. We have made some progress with pre-laboratory instruction, our purpose being to demand that the student has thought through the background or theory of an experiment before entering the laboratory. We do not see at the moment how laboratory work itself can be programed except for essentially foolproof procedures where the answers are completely known. Programed laboratory work runs counter to another trend in laboratory instruction, which emphasizes the investigative approach and is based on the premise that the greenest freshman may, by careful observation, discover something new. Some programing work currently being carried out at Earlham in the Chemical Bond Approach (CBA) Project suggests that a simple experiment with a prescribed kit might be used as an introduction to the development of classroom material. Thus a set of electrostatics experiments may serve as a first-hand basis for the development of electrostatic concepts.

It is of interest to note that we have become more convinced of what should be obvious to all chemistry teachers, namely that learning in chemistry cannot proceed very far without knowledge of the physical system, without laboratory experience.

Preparation of Programs

Our programs so far, except for the recent ones developed in the CBA Project, have been of the Skinner or linear constructed response type. Their general

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[1] Grant No. 7-12-026.00, United States Office of Education, Department of Health, Education, and Welfare.

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nature has been described by Young.[2] We have kept open the question of an optimum error rate, being concerned not to make the steps so simple as to insult the student's self-respect. We have used programing more for the exercise of logic than for simple memorization. If something has to be memorized, apart from a few mnemonic aids, we doubt if we can provide much help on the college level. We think that much direct memorization can be bypassed by supplying and using the terms to be memorized often enough, so that the student will know them without conscious effort.

We are beginning to see uses for multiple choice forms of answers and for branching and looping programs, that is, the supplying of further instruction to students who missed a given frame; and we will probably attempt combinations of multiple choice and constructed response items in the future. We would insist that the value of constructed responses is that the student supplies the answers. Instructors who give only multiple choice examinations are likely to lose any conception of the number of different ways his students can go wrong. We detail below some of the information obtained from an analysis of student responses.

The most common procedure for preparing programs has been the following:

(1) The separate items are typed on pages of 4-in. × 6-in. paper pads. Having items on separate pages permits easy replacement or addition of further items.
(2) The program is checked by two or three students.
(3) The program is checked by one or more chemistry colleagues.
(4) It is revised, possibly rechecked, and mimeographed in linear sheet form.
(5) The mimeographed program (to be used without machines) is submitted to one or more classes for testing.
(6) Erroneous answers are listed and analyzed, and error rates are computed and plotted.
(7) Items are analyzed in the light of comments and test results, and a revised version is prepared.

In the development of programs it is important to know accurately what the student knows before he works through the program and what he has gained by the process. The written responses are usually insufficient to pinpoint the difficulties. Often, questioning of students who have worked through the program will help but pre- and post-testing is necessary and in the development of the programs ought to be extensive. Where possible, we feel that the program should be tested also in another institution.

Aids to Effective Chemistry Teaching

Assuming that in principle programed instruction is a useful teaching aid, responses from individual students and error rate data can be used to improve such instruction by expansion, correction, and the removal of ambiguities. A program on oxidation-reduction equations originally had an average error rate of 9% (tested on 30 sophomores). After revision the following year, a class of 25 sophomores supplied answers with a 7% error rate, which may be a chance variation; but the error rate for the last ten items dropped from 15 to 4%.

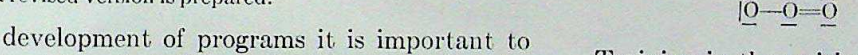
When the same program was given to a group of freshmen, however, the error rate was considerably higher (16%). This may only be due to the broader range of students involved but it may indicate that something like general chemical maturity and greater ease in handling a technical language are significant in learning materials for which both groups were thought to have an adequate specific background.

Programing forces the teacher to become aware of the complexity and inner logic of a topic he may have thought of as simple and straightforward. Thus the idea of formal charge, on which perhaps half an hour is usually spent in class, and which students notoriously do not master, required the following concepts for its systematic presentation:

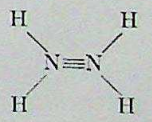
structural formula charge
concept of "formal" charge as a first approximation
shared electrons concept of equal sharing
algebraic sum of positive and negative charges
proton, electron, nucleus, atomic number, nuclear charge
inner shell atomic kernel kernel charge
Lewis structures (showing only outer "valence" electrons the atomic symbol standing for nucleus plus inner complete electron shells)
law: sum of formal charges = charge on particle as a whole (zero for molecules, ionic charge for ions)
lines to represent electron pairs: alongside atom symbol if unshared, directed away from atom symbol if shared.

The above list of concepts was used in a program of 40 frames designed to teach the student how to calculate formal charges when the detailed electronic structure was supplied. Instruction in the writing of such structures involved another 47 frames and required a further set of concepts.

The formal charge program was remarkably successful. In an unannounced post-test sprung on the students a few days after completion of the program, with no instruction or discussion of the subject whatsoever, 21 out of 23 freshmen gave the correct formal charges for the atoms of



Training in the writing of Lewis structures was not so successful. In a question in the same post-test: "Write the electronic formula, showing both shared and unshared outer electrons, for hydrazine, H_2NNH_2," 14 out of 23 students gave the correct answer. The others gave the identical wrong answer:



The rule of two seems to have been learned, the octet rule not at all. Here seems to be an ideal place for a branching program!

Some teaching problems are highlighted by programs but are not easily solved by program revision. Figures 1 and 2 show the error rates for a program on the systematic naming of alkanes given to freshmen at Earlham College and in the nursing curriculum of the University of Illinois at Navy Pier respectively.[3] Item 11 which stands out in both figures was ambiguous and was easily corrected. Items 33 and 35 on the other hand were the most difficult naming problems, but were thought to

[2] Young, J. A., J. Chem. Educ., 38, 463 (1961).

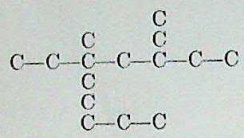
[3] We are indebted to Professor Joan M. Jones of the University of Illinois at Navy Pier for supplying this information.

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be solvable on the basis of earlier instruction. It may be of interest to notice that whereas the general error rate in Figure 2 exceeds that in Figure 1, the error rates for items 33 and 35 are markedly lower in the second case. This is probably evidence for something many have suspected, that the making of mistakes helps in the learning process if the errors are immediately recognized, and that a more difficult program with which a student has to struggle will teach him more than one he can breeze through. A student who skims over the preliminary material is likely to find difficulty with a later item requiring the use of much of the earlier information.

Clearly the error rates for items 33 and 35 were too high. Item 33 asked for the Geneva name of the hydrocarbon whose skeleton is

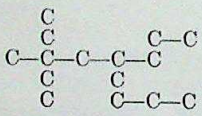


In place of the correct answer (5-methyl-3,5-diethyldecane) some erroneous answers read:

5-methyl-3,5-ethyl-	(3 students)
3-ethyl-5-methyl-5-ethyl-	(2 students)
3-ethyl-5-methylethyl-	(2 students)
5-methyl-3-ethyl-5-ethyl-	(3 students)

In addition three answers were based on heptane as the parent hydrocarbon and three on octane. There were 29 student responses in all. Clearly the problem here is the application in the right order of a series of detailed and somewhat arbitrary rules. The names listed above are all unambiguous; they can only refer to the substance represented by the formula, but they are not the correct name. Reference works do not list them.

Something was learned from the mistakes here, for in the last item, asking for the formula of



the error rate was down to 14%.

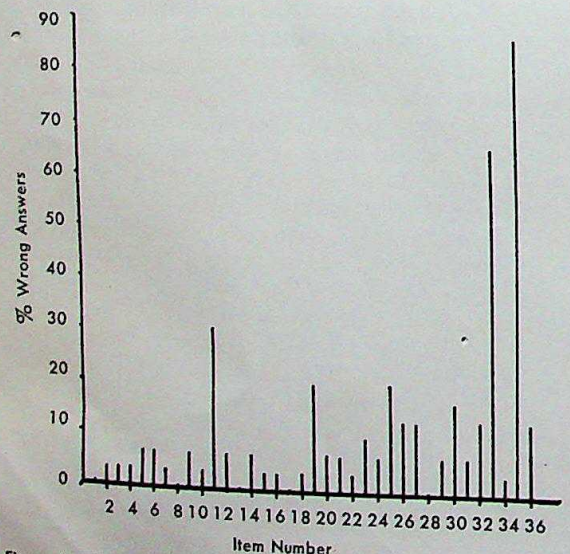


Figure 1. Error data for a 36 item program on the nomenclature of alkanes tested on 29 students in a liberal arts college.

Item 35 asked for the name of $(CH_3CH_2)_4C$. Eight out of 29 students left it blank, four simply called it nonane and the total error rate was 86%. The responses to a number of other questions have led us to believe that one of the difficulties students face in organic chemistry is the deciphering of such condensed formulas.

In the revision of the alkane program an attempt was made to lead up to the most complex items more slowly and to emphasize the process of deciphering. The attempt was only partially successful. The error rate for the diethylpentane item dropped from 86 to 65%. The 5-methyl-3,5-diethyldecane frame was made the last item in the program where it was missed by 73% compared with the earlier 65%! There may be a real problem in using linear programing for "synthetic" conceptual learning, the combining of items of material from many different points in the program.

We have found programing so far most satisfactory in very tightly knit subject matter, connected by logic, arbitrary rules, or both. Correct word answers seem to be elicited with much greater difficulty (unless supplied in the same or the previous frame) than numbers, symbols, formulas, and proper names (as in naming systems). If one can generalize from our experience one might predict that linear programs requiring written responses are likely to be most successful with mathematical topics or subjects that can be put in symbolic form, i.e., that are amenable to the approaches of modern algebra.

One of the widely-advertised advantages of self-instruction is that it is truly individualized instruction. We have become convinced that if this advantage is to be obtained it is folly to expect one program to teach a given body of material to all students of whatever background and intelligence. Programs are individualized instruction only if they are designed for a particular group of fairly homogeneous students. Self-instructional devices do not automatically circumvent the problem of boring the bright student and passing by the dull or ill-prepared student by a presentation designed for the average student.

In summary, our admittedly limited experience suggests that reasonably short programs on specific topics

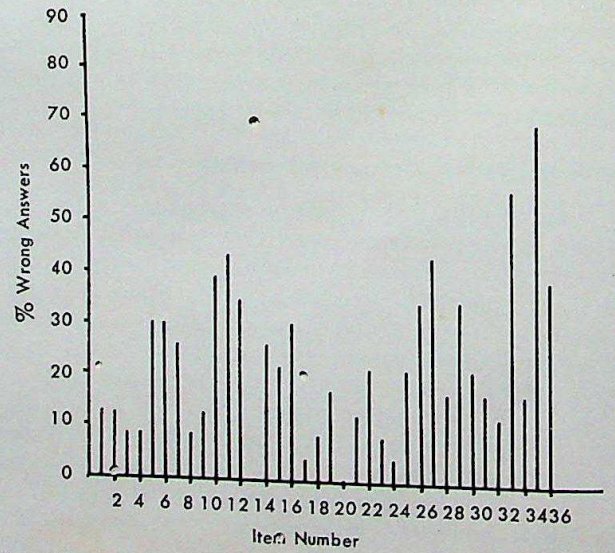


Figure 2. Error data for the same program as in Figure 1, tested on 23 students in a university nursing curriculum.

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would appear, on the basis of student and faculty comments, to be the most useful approach to college chemistry programing. This means that programs would not replace a conventional text entirely, but would replace the text (or possibly be used in conjunction with the text) for certain topics. Student comments on programs seem to be generally favorable. There is some complaint about the tediousness of working clear through a unit. Yet, in spite of this, students apparently feel it is a useful technique because they have been asking for more units on other topics with which they have difficulty, such as equilibrium, activity coefficients and resonance.

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The Use of Programed Instruction at the Air Force Academy

The United States Air Force Academy, in keeping with its aim to remain among the progressive colleges and universities of the nation, has an active interest in the use of auto-instructional devices. Our over-all objective is to discover and develop the most effective presentation for any given learning situation. We view programed instruction as one part of the complete array of instructional devices and techniques.

During the past year, programed instruction has been used for courses in statistics, algebra, English, and for remedial work in these and other areas. The first course in aerodynamics is presently being taught over closed-circuit television by what might be described as "oral programing." Each student has a switch which he uses to indicate his answer to key questions asked by the instructor throughout his lecture. The instructor has a device which records the number of correct answers and allows him to gauge the class's understanding of each important point. Programed workbook exercises are used after the television presentation to reinforce the lecture. Mastery of the subject is measured with a programed examination.

An intrinsic program covering part of the first semester course in general chemistry will be used for the first time this fall.[1]

A basic premise is that programed instruction will teach the subject successfully. The test is to determine its effectiveness compared to present methods. Intrinsic programing is being used for nearly the same reasons that were cited by Dr. Day.[2] We feel that it is better adapted to the presentation of subjective material and that it holds the student's attention better. Intrinsic programing is also better suited to review and to a rapid overview by the student who already has some knowledge of the subject. All he needs to do is read and answer the questions. When he makes an error, he can go back and read the explanatory material. Therefore the programer must make certain that his questions cover all essential items of information.

The objective of the autoinstructional program is to combine the material which is contained in the textbook (Selwood)[3] and study guide. It is a complete source of material rather than supplementary drill. In this respect it differs from the majority of currently available programs in chemistry.

The program will be used in the fall '62 term by about 100 cadets of varying abilities. Since the experimental use of the program cannot be allowed to jeopardize the eventual performance of the cadet, we decided to write our own program and tailor it to the course. During the test period, the cadets in the experimental group will use only the program. They will not read the textbook nor do the normal study guide assignments. They will attend class periods for the purpose of using the program and will spend whatever additional time they need outside of class. Some of the more important static demonstration devices such as the spectroscope and conductivity apparatus will be set up in the classroom. At the proper point, the student is directed to examine them. An instructor will be on hand to answer questions and assist students who have difficulty. They will attend laboratory periods as usual.

The regular presentation of the course follows the chapter structure of the textbook very closely. Consequently, the program was written to contain the material in each chapter. Needless to say, material was rearranged and amplified in some cases.

My approach to programing and some of my experiences may be of interest. All of the right-answer

Presented at the Symposium on Programed Instruction at the 124th Meeting of the American Chemical Society, Atlantic City, New Jersey, September, 1962.

[1] Our chemistry classes are divided about 3 times each semester into sections of 11 or 12 cadets. Sectioning is on the basis of performance in the course up to the date of sectioning. During each sectioning period a single instructor conducts both the classroom and laboratory work for each section. He reads and corrects all homework assignments, lab reports, quizzes, and examinations. In short, one individual is responsible for the cadet's entire experience in chemistry for a period of about six weeks. The primary instructional materials are the textbook and a study guide which contains written assignments designed to emphasize the important topics covered in the text.

Little time is devoted to straight lecture. Instead, classroom discussion centers on student questions which arose during the previous evening's study. A short quiz is used to evaluate the cadet's mastery of each chapter of the textbook. There are also mid-term and final examinations.

[2] See previous paper in This Symposium, THIS JOURNAL, 40, 18 (1963).

[3] Selwood, P. W., "Chemistry," 3rd ed., Holt, Rinehart, and Winston, Inc., New York, 1959.

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frames were completed in sequence in order to preserve continuity of thought and presentation. It is harder to achieve a logical presentation in intrinsic programing than in linear programing since each step is somewhat larger. Another difficulty is in limiting the amount of material which is included. It is very tempting to cover every subject in depth. A conversational quality can be maintained by imagining that the student is right in front of the writer. It is helpful to imagine the student's reply as well. I think it is very important to use a correct vocabulary. Clarity and conversational tone are not preserved by the use of slang. For example, "decompose," is used not "break down." A molecule is a particle of matter, not a chunk or a piece.

As soon as the first draft is complete, it is read by another chemist and by an editor who does not have a scientific background. The chemist checks facts. The editor judges the readability and can often make valuable suggestions for improvement of the work. A good editor can do a great deal to preserve the conversational tone of the program.

Incorrect responses were chosen on the basis of my experience with the student population. Since it was impossible to test the program piecemeal as it was written, there was no other choice. I do plan to prepare part of the copies of each chapter with the responses blocked out. Each student will construct and write his own response before looking at the choices provided for him.

The wrong-answer frames were written after the completion of the right-answer sequence for an entire chapter. It is here that an intrinsic program stands or falls. The student reaches these pages by honest mistakes. A successful program must explain his error and give him additional help. It must not merely repeat the original information. A valuable technique here is to assume that the chosen answer is correct and to examine the consequences of the assumption. Many times another illustrative example can be cited. In any event, the student must be made to feel confident that he will not repeat his mistake.

The scrambling of the program can be done in a number of ways. I prefer to divide each chapter into three or four "blocks" before scrambling. This has two advantages. The first is that it keeps the number of pages which must be turned to a minimum. It also will allow the program to be broken up into topics for remedial or review work. I also attempt to have the choices on each question in order of increasing page number (see Figure 1). The disadvantage of wasted space can be overcome to a large extent by placing more than one frame on a book page whenever possible, (see Figure 2). One must bear in mind that not all correct responses can be "A" or "B" frames, but that there should be a random mixture of the two.

Finally, an index and glossary of important terms are prepared. The index contains all the major concepts and terms contained in the chapter. The glossary is a handy reference.

The total number of pages is from $3^1/_2$ to 4 times the combined total of textbook and study guide pages.

What are the qualities of a good programer? He must know the student population for whom he is writing as well as the objectives of his program. He

page 23A
from page 19B

You are correct. If the point of equilibrium for the dissociation lies to the right, HA is a strong acid.

Usually mentioned in the same breath with acids are *bases*. There are many ways to define a base. For our purposes, it will be sufficient to say that a base is any substance which is capable of providing the hydroxide ion, OH^-, in a solution. Most bases dissociate completely when they dissolve in water and are, therefore, strong bases. Typical bases are sodium hydroxide, NaOH, potassium hydroxide, KOH, and calcium hydroxide, $Ca(OH)_2$.

One of the few weak bases which you will encounter in this course is ammonia, NH_3. At first glance, you might wonder how NH_3 could provide OH^- ions in a solution. It does this by reacting with the water as follows:

$$NH_3 + H_2O \rightarrow NH_4^+ + OH^-$$

At one time, it was thought that the compound NH_4OH was formed which in turn dissociated. However, current thinking is that the above reaction most clearly represents the actual situation.

As you can see, the presence of the solvent water is an essential part of the definition of both acid and base. This is because water itself dissociates into hydronium and hydroxide ions as represented by:

$$2H_2O \rightarrow H_3O^+ + OH^-$$

This equilibrium must be considered whenever water is present, either alone or as a solvent. We'll see some of the consequences of this in a moment. First, choose the true statement from the three below.

Water is both an acid and a base	*Page 18B*
Water is only a base	*Page 21A*
Water is only an acid.	*Page 24A*

Figure 1.

page 32A
from page 29A

You are incorrect. Although you may not be able to give the reason, there are sufficient facts to enable you to tell whether or not the solution will conduct electricity.

The basic fact is this: All solutions which give unusually large freezing point depressions also conduct an electric current.

The question, then, is: When a 0.25 m solution freezes at $-0.90°C$, is it giving an unusually large freezing point depression?

What's the answer? To get the normal freezing point depression you can use the equation.

$$\begin{aligned}\text{F. P. Depression} &= (\text{m})\,(\text{molal F. P. Constant}) \\ &= (0.25\text{ m})\,(1.86°C) \\ &= 0.46°C\end{aligned}$$

The normal freezing point depression is expected to be 0.46°C. The actual freezing point depression is 0.90°C.

Return to page 29A and select another answer.

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page 32B
from page 25A

You are wrong. Na is not a cation. It is not an ion at all. Ions are particles which bear an electrical charge. Positively charged ions are called cations (cat'-eye-uns). Negatively charged ions are called anions (Anne'-eye-uns). The charge on an ion is indicated by a superscript written after the atomic symbol. For example, Na^+ is a cation, while Br^- is an anion.

Return to page 25A and choose another answer.

Figure 2.

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must also be able to test his product. I think he should be a subject matter expert and an experienced instructor as well. The well qualified teacher in the school or on the campus meets these requirements. The only other qualities needed are an interest in programing and the ability to write simple, lucid prose. Careful editing can overcome a lack of the latter to some extent.

Assuming that this year's test is successful, future plans call for the expansion of the chemistry program to include the entire first semester. Some 8 mm silent motion picture films of demonstration experiments will be produced. They will be put in cartridges for use with the Technicolor 800 projector. Individual projectors will be made available for each student so that the demonstrations can be inserted at the exact point of the program where they will give maximum impact.

It is possible that portions of the course will be written in "oral programing" similar to that being used in aerodynamics. There are indications that this can be done in less time than conventional programing.

Acknowledgment

The assistance of Major Franklin C. Butler, Jr., in the preparation of this paper is gratefully acknowledged.

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Programed Instruction in High School Chemistry

The high school chemistry course is designed to meet the needs of the person for whom this will be the only formal instruction in chemistry in his lifetime. It should give the student some understanding of what chemists believe about the nature of matter and energy, and why they believe these things to be true. At the same time the course provides some understanding of practical matters like storage batteries and plastics. On the other hand, the high school chemistry course should provide a solid, systematic introduction to chemistry for those students who plan careers in chemistry, engineering, the physical sciences or medicine. At Niskayuna High School chemistry students vary as widely as do the aims of the course. They range in age from 14–18 years since they are not divided according to grade in school.

It was for this diverse student population that the author wrote a linear program on the calculation of molecular weight. The format was simple; it was a paper and pencil program. The confirmation or correction of the student response was provided for by a cardboard mask. The results of these first programs substantiate what other investigators have found.

To review these findings, first, there is a wide variation in the time it takes students to complete a given set, 21 minutes to about one hour. This reflected a difference in speed of reading, in mathematical ability, and in study patterns. The girl with the 21-minute time has very quick reflexes. The boy who took an hour is deliberate in all that he does and is also a poor reader. He was in serious difficulty in the course because he could not maintain the class pace. Programed instruction permits the student to work at his own best rate instead of being paced by the teacher or by the fastest student in the class.

Secondly, students mastered programed material better. Several days after the experience with programed instruction and with no further treatment of the calculation of molecular weights in class, the students took an unannounced quiz. The results of the quiz showed that grades were up 15–20 points. Some students made 90's for the first time in the course. Mastery of material is probably better because the student proceeds in small, logical steps. The program was also designed to give practice (or drill) in a sufficient number of problems so that the students were sure of the method and principle. They could not say "I have the general idea." Programed instruction helps to assure the teacher that assigned work is done and understood.

The students were asked for comments and evaluation of this method of teaching-learning. In general they responded well to the use of programs. It was not simply due to its novelty, for interest remained high in the subsequent sets they used. Comments ran, "I could see I was learning something." "I liked it because I didn't have to wait for anyone else." "If I didn't understand something, I could stop and go back and not get lost." "It was fun. It felt good to know you were right." "You don't get a chance to practice your mistakes. If you are wrong you know it and know why right away." "You don't make the same mistake twice." And this remark which is an interesting comment on the lecture method, or the instructor, "It makes you pay attention. You have to answer or quit."

One negative comment came from a very able student. "The programs stifled my own way of thinking. I had to do it the program's way or not at all." This criticism or reaction is given occasionally by the mature student.

Presented at the symposium on programed instruction at the 124th meeting of the American Chemical Society, Atlantic City, New Jersey, September, 1962.

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Programed instruction can be particularly valuable for the poorer student. The programs were used with average, honors, and slower students. Niskayuna High School offers a course called Physical Science which is planned to give the nonacademic student some understanding of the principles of physics and chemistry with little mathematical treatment. A colleague used programs on symbols of the chemical elements, calculation of molecular weight, and calculation of percentage composition, with these classes.

She found that the students learned more and made higher grades than similar students had ever done before. In addition, they preferred the method of programed instruction. In working through the programs they had the satisfaction of succeeding in school, an experience that they had seldom had before. It did take them longer, but they could learn. Programed instruction is thus a valuable tool at the lower end of the learning spectrum. By this method students who are slow learners have a patient tutor with unlimited time.

The original program and additional ones have since been revised and retested. The author can confirm what others have found to be the benefits to the person who writes a program. The teacher gets immediate feedback on which items are poor, pointless, or ambiguous. If 50% of the students make an error on item 16, there is nothing wrong with the students, but with item 16.

The teacher becomes more self-aware. He recognizes that areas of instruction which are difficult are probably so because the teacher assumes the students know something which, in fact, they have not been taught. Or the teacher sees that his presentation of ideas and information is in too large blocks, or that misconceptions are not being corrected as they arise. The instructor perceives, after writing a program, why his successful presentations have worked and becomes aware of the source and nature of his failures. It is an illuminating experience.

After writing the first few programs and finding their value, the author envisioned programing the entire course in high school chemistry. It is not clear, however, that this is possible or desirable in the present state of the art. As programed instruction is practiced today, it is a supplement to the live teacher and cannot substitute for him. In addition, programed instruction tends to deal only with verbal skills and ignores the laboratory and manipulative skills which are an important part of the course.

Another reason that instruction on the high school level cannot be entrusted to programing exclusively is that most students of this age need human contact in the educational process. On the other hand, for certain students the relative impersonality of programed instruction may provide a better learning situation.

In certain topics which are simple and straight forward such as the calculation of percentage composition, programed instruction can do the whole job—introduce the subject, teach the method, and provide a self-test for mastery. It is excellent for teaching students how to solve specific types of problems.

Programs also can teach relations among facts and provide for sufficient drill so that mastery is assured, for example, in a study of the relative reactivity of the halogens. Thus programed instruction in high school chemistry can be used to teach *what* and *how*. Programs can also be used to teach the *why*, although it is much more difficult to write such programs. Considerable skill and experience are required to write a successful program for deductive reasoning. Programed instruction can marshal the relevant information, pose the critical question, and confirm or correct the student's own deductions. It can help him find out for himself. Ultimately, of course, he must learn how to collect the data, and formulate the questions for himself. This too, can probably be programed. The possibilities of this method are just becoming evident.

Working through a program can be assigned as homework, so that the teacher is confident of uniform mastery of minimum materials by the student before class discussion begins. Programs can also be used for review, for testing, and for remedial work. A student who needs additional help can be given a program to do on his own, saving time for the rest of the class and the instructor. Last year programed instruction enabled a student who was out for 5 weeks to stay up with his class.

In summary, programed instruction in high school chemistry provides an additional tool for learning the what, the how, and the why. It can be used to introduce, teach and self-test certain topics. It can be used for homework and for remedial work. Another important value is that it forces active participation by the student in the teaching-learning process. It shifts the responsibility for learning back to the student, where it should be. Because it provides for a self-pacing logical sequence of small steps, and immediate confirmation or correction, it helps solve the problems created by the wide spread of abilities and interests among high school chemistry students.

Surplus Science Equipment Available for Health and Educational Institutions

A variety of useful equipment and material is available at practically no cost to institutions through the donation of the Surplus Property Utilization Division of the Department of Health, Education, and Welfare. Material appropriate for science teaching from elementary school to college level is available. A list of directors of State Agencies for Surplus Property to which inquiries and requests should be made is available from the USHEW office, Washington 25, D. C.

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Irwin Cohen and
Robert Fetterolf[1]
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Programed Instruction in Qualitative Analysis Laboratory

Two of the three basic ideas of programing, careful and patient development of the subject and personal involvement by the student, are already included in the usual course in qualitative inorganic analysis to the limited extent that there is an orderly sequence of the analytical groups and personal involvement in the laboratory unknowns. However, the sequence of groups is not an orderly introduction to the principles of analysis, and the personal involvement is directed toward solving the unknowns rather than toward understanding the method of analysis. With these difficulties as the point of departure, the qualitative inorganic course has been found to be well suited for a trial of programing in the laboratory.

We would like to start the student with the idea of doing one thing at a time. However, even the simplest analytical groups involve not one but several distinct principles. For example, the cation group silver, mercury(I), and lead involves the group precipitation, the variation of solubility with temperature, complex ammine formation and its reversal through acid-base neutralization, and a redox disproportionation with the appearance of a basic amide. From the viewpoint of programing, this is much too much. It is even, perhaps, disorderly, or at least so appears to the student. Therefore, adherence to sound programing principles means that we should abandon the analytical groups as the units of instruction.[2] Just as we do not teach organic or inorganic chemistry by following the flow sheets of industrial production, so also we should not teach qualitative analysis by following an analytical sequence. What we ought to do is to develop an analytical sequence by way of a pedagogical sequence, based on principles rather than on groups. We ought to teach the principles of analysis rather than a particular scheme of analysis, so that a student then can follow intelligently any given scheme and, when the occasion arises, devise his own.

A first principle in qualitative analysis is solubility. The starting point in this principles approach should therefore be a group of substances that can be differentiated by solubility considerations alone. One possible starting point is the four substances composed of the sodium, calcium, chloride, and carbonate ions. (Calcium carbonate is insoluble, and of the three soluble substances, calcium chloride forms a precipitate when its solution is mixed with one of sodium carbonate, a solution of sodium carbonate forms a precipitate when mixed with calcium chloride, and sodium chloride forms no precipitate with the others.) An unknown from this list would be too easy a problem. This points our attention to the second difficulty in the course and introduces the second change in constructing the program.

The laboratory part of the traditional course is concerned with the work of the technician rather than with that of the chemist.[3] So, before asking a student to identify an unknown, we ask him to *find out how* to identify it.[4] The laboratory work thus changes from the technician's approach, learning a scheme of analysis, to the chemist's approach, learning how to devise a scheme of analysis. It is not enough only to ask the student to devise his own scheme; he should also participate, through programing, in the study of the techniques, reasoning, and principles by which a scheme is set up. It is the combination of this chemist's approach with the principles approach that results in a programed course.

The program we have developed (chiefly in the second semester freshman laboratory in the course for liberal arts students) at present consists of nine steps. First, given four substances as known solids, the student experiments with them to find out how they can be differentiated, and then identifies an unknown by his own procedure. On finishing this, the student's answer—his unknown report—is checked. If he is right he can confidently proceed further in the same manner; if there is an error, it is discussed with the instructor before going on. In practice, mistakes are rare.

The next steps are, (2) solutions of the four substances; (3) nine substances—three cations, three anions; (4) more than one solute in an unknown; (5) five cations, five anions; (6) the given ions in the presence of new, unknown ions; (7) development of the chloride and sulfide cation groups; (8) ten cations, five anions; and (9) addition of new, unfamiliar ions to an unknown which also contains some ions which the student has already studied.

For example, in the second major step, the student devises his own scheme for differentiating solutions of four ions (studied in the first step) from each other and

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[1] Present address: The University of Florida, Gainesville.

[2] Suggestions for alternatives to an analytical scheme as the basis of instruction have been made, for example, by R. Battino, Abstracts of Papers, American Chemical Society Meeting, September, 1960, p. 15f; Benedetti-Pichler, A. A., Schneider, F., and Steinbach, O. F., this Journal, **34**, 381 (1957); Frank, R., this Journal, **34**, 383 (1957); Strong, F. C., this Journal, **34**, 401 (1957); Vasilakes, W., this Journal, **38**, 146 (1961); and Fowles, G. W. A., this Journal **39**, 401 (1962).

[3] See, for example, in this Journal, Summerbell, R. K., **31**, 365 (1954); and Summerbell, R. K., Lestina, G., King, L. C., and Neuman, H. M., this Journal, **32**, 475 (1955).

[4] An important step in this direction was taken by Battino, *op. cit.*

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from water. As the number of ions to be distinguished is increased in the remaining several major steps, other complexities are carefully introduced, and the student is taught, one by one, how to deal with each of these. (This, obviously, requires careful selection of the new "unknown" ions selected as the added ions, as the procedure becomes more complex.) Examples of new concepts which are learned, one at a time, are: the importance of the order of addition of test reagents, the reliability of the evidence which indicates the presumed presence, or absence of an ion; interfering ions; the convenience of separate testing for anions and for cations; the concept of a weak acid; ionization equilibria; *p*H; confirmatory testing; Brønsted acids and bases.[5] Special techniques such as paper chromatography, flame spectroscopy, handling of solids; and other similar concepts may also be introduced.

The third basic idea of programing is immediate reinforcement, by the inclusion of answers within the program. In a laboratory program, however, answers are immediately given, not by the written work but by the test tube, although hints do need to be given to avoid misinterpretation or to improve technique. In programing qualitative analysis, the unknowns are a major factor; they are easy to grade quickly and any errors can be checked over and discussed with the student. In the verbal parts of this program, answers are not written in (as they are in a linear program) but rather the student checks his work continually with the instructor. This is possible and probably advisable here because the program is intended only for class work in the laboratory rather than—as most programing is—as a private tutorial aid. Furthermore, it is desired here to emphasize the laboratory work as an experimental rather than a verbal study. For the same reason, the theoretical background, which is of course necessary in the full course, is not included in the laboratory program. All verbal parts are held as much as possible to a distinctly supplementary role.

It may be questioned whether this application of programing should indeed be called programing, since the answers to the questions are thus not supplied in the written program itself for immediate checking. To us, the form of the answers, visual or oral or written, does not constitute an essential difference. Of course, confirmation of the student's answer, which is given by the instructor, is not generally as immediate as the answer given in the usual form of programing. The question is, how immediate must the answer be confirmed for effective reinforcement? The answer to this must be supplied by psychology, but it is suggested here that as long as a program is written so as to elicit close to 100% correct answers, the verification may perhaps wait for several minutes or longer without serious harm.

The verbal parts of a laboratory program such as this could in fact be written in the usual manner, although it would not then be so easy to integrate them with the laboratory parts. A laboratory program in itself always has its own immediate reinforcement through events occurring in the test tube. The difference between a programed laboratory instruction and the typical laboratory class lies principally in the conversion of a collection of individualized but impersonal demonstrations into a careful and patient development of principles in which the student is a participant instead of an observer.

This experiment in programing has been developed over a three-year period. The maximum use so far has been 24 laboratory hours. No attempt has been made to measure the results by a statistical analysis, nor is it suggested that the program is already perfected or is a finished course in qualitative analysis. But we feel that it is a sound introduction. Throughout the program, it is inevitable that some students make false starts and waste time on blind alleys. But they enjoy it. They are discovering things. They can see their progress as an analytical scheme emerges and as they find that they are able to master the continually expanding list of ions. In contrast to the usual course in which there is a slow start with many unknowns coming later, here the students solve two unknowns in the first two hours of work and then proceed more slowly as they see and seek to understand the growing complications. The steps throughout are small enough for them to find their own way, and they are personally involved in what they are doing.

The freshman students, the instructor, and the senior student who scouted the way all enjoyed the work, learned much about analytical chemistry, and exercised greater initiative and imagination than would otherwise have been the case. Laboratory programing is feasible and rewarding both for the class and the instructor. It is hoped that those who have not yet tried it will do so.

Acknowledgment

The authors are indebted to Prof. Young for several important suggestions on the presentation of this paper.

[5] Detailed descriptions of the analytical procedures involved in the nine steps can be obtained on request from Cohen. Briefly, each of the nine steps is composed of a series of smaller steps, in which the student is directed to carry out laboratory studies not unlike, in its use of explicit directions, those found in some laboratory manuals for elementary chemistry. The difference lies in what is done by the student as a result of his observations when the directions are followed.

Erratum

The word "density" was omitted from the third paragraph of the article "The Cesium Ratio" by Jack Eichinger in the October issue (THIS JOURNAL, **39**, 536 (1962). That paragraph should begin as follows:

"The 'cesium ratio' is defined as *the ratio of the ionic charge density of any real or theoretical ion to that of the cesium ion.*"

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An Experimental Program on Chemical Equilibrium

Teachers of freshman chemistry today find it increasingly difficult to satisfy the varying needs of students, whose previous experiences range from excellent high school chemistry courses to no training at all. In addition, the rapidly increasing student population and the resulting large classes essentially exclude all forms of teacher-student interaction other than formal lectures. Assigned readings and films help to buttress the lecture material, but must also be regarded as passive methods of learning, whose inefficiency is demonstrated by the poor performance of many students.

Since programed instruction requires the active participation of the student in the learning process, it can be used to alleviate these problems. Since each student can work at his own rate, repeating sections if necessary, it can accommodate a wide range of abilities. The program reduces the differences between students by bringing all of them up to a minimum standard. With the tedious and time-consuming drill work accomplished for him by the program, the teacher can use the lecture to build on this fundamental knowledge and discuss more advanced topics according to his own interests and those of his students.

Our program on "Molecular Equilibrium," now in its final testing edition, is the first of a series which will cover the subject matter of general college chemistry. Equilibrium was chosen as the first topic because most students find it difficult, and it therefore offers a challenge to the programer and presents an excellent opportunity to develop good programing technique.

Organization of the Program

The program is arranged in three parts: (1) the law of chemical equilibrium, (2) equilibrium changes, and (3) equilibrium calculations. Each part consists of many small sections whose titles correspond roughly to paragraph headings in a textbook; in the part on equilibrium calculations, each problem is a separate section. This arrangement makes it easy for the teacher to view the content of the program and adapt it to his needs. It also helps the student to locate specific topics for study or review.

The program is designed so that over 80% of the students will answer a given frame correctly. If a student's answer is wrong, he will only have to review a few frames to find his error, for the logical sequence of steps will not allow him to progress very far without comprehension. A series of three typical frames in the program are presented in Figure 1.

Presented at the Symposium on Programed Instruction at the 124th Meeting of the American Chemical Society, Atlantic City, New Jersey, September, 1962.

Testing the Program

In order for the program to be effective, the size of the steps taken by the student in moving from one frame to the next should be fairly uniform. Moreover, the steps should be neither so large as to produce a high probability of error and thus discourage the student, nor so small as to unnecessarily lengthen the program and increase the time required to complete it. In testing a program, the percentage error for any given frame can be taken as a measure of the step-size for that frame.

Before testing the program on a large scale to determine the step-size, it was reviewed by a few interested students at Albion College to detect major errors and inconsistencies. Even one or two students can indicate which frames need to be reworded, and which areas of the program are vague or misleading.

The program was revised and then tested on a group of approximately 300 freshman chemistry students at Michigan State University who had received no previous lectures on equilibrium. From the completed programs, the percentage error for each frame was determined. Since the optimum percentage error for

A. The reversible reaction

$$A_{(g)} + B_{(g)} \rightleftarrows C_{(g)} + D_{(g)} + \Delta$$

is allowed to reach equilibrium. If the temperature is increased, i.e., heat is (removed, added), Le Chatelier's Principle states that the system must adjust to ———— heat.

A. added / absorb

B. When the forward exothermic reaction occurs: $A_{(g)} + B_{(g)} \rightarrow C_{(g)} + D_{(g)} + \Delta$ heat is (absorbed, evolved). When the reverse endothermic reaction occurs: $C_{(g)} + D_{(g)} + \Delta \rightarrow A_{(g)} + B_{(g)}$ heat is (absorbed, evolved).

B. evolved / absorbed

C. To relieve the stress of an increase in temperature on the reversible reaction: $A_{(g)} + B_{(g)} \rightleftarrows C_{(g)} + D_{(g)} + \Delta$ heat must be ————. Therefore, it is the (forward, reverse) reaction which is favored.

The formation of (reactants, products) is favored.

C. absorbed / reverse / reactants

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frames in programed instruction has not been established, it was arbitrarily set at 5–20% for this program. All frames with percentage errors outside this range were reviewed. Frames with over 20% error were reworded or replaced by two or more frames to decrease the step-size. Some frames with percentage errors less than 5% are unavoidable, but when several of these appeared in a row, the step-size was increased by eliminating some frames.

Evaluation of the Program

The only criterion by which the worth of a program can be judged is its success in teaching the student. Unfortunately, time and circumstances did not permit us to administer a post-test to evaluate the effectiveness of this program. We felt, however, that it would be useful to obtain the student's opinion as to the value of the program. See Table 1. There was surprisingly little variation in the evaluation of the program by students of different abilities. Their reactions were uniformly favorable: 80% or more of the students in each group felt the program was effective. The high percentage of "A" students who approved of the program was particularly gratifying, since we had expected opposition from this group.

By far the greatest objection to the use of the program was the time required to complete it. The amount of time reported ranged from 3 to 12 hours, averaged about 6 hours. The present edition of the program is somewhat shorter, and it is expected that additional testing will abridge it further.

The students were particularly critical of errors in the program. Most of the errors were typographical, but their presence is a legitimate cause for complaint. Errors are far more serious in a program than in a conventional textbook. For a program to be effective, it must be absolutely reliable, since even one wrong answer can disrupt an entire sequence and cause confusion.

As expected, a few of the students objected to learning by programed instruction. These students should be offered textbook references which cover the same material as the programed assignments. Certainly, programed instruction is not the only method of learning, and not necessarily the best one for all students. It is believed, however, to be an effective teaching aid, and an excellent method for the great majority of students to obtain a strong foundation in the subject.

Table 1. Evaluation by Students

	Grade in previous chemistry course	Number of students	% of students giving positive answer to question (A)[a]	% of students giving positive answer to question (B)[b]
Non-repeating students	A	22	86	90
	B	80	80	70
	C	93	82	80
	D	15	80	100
Total non-repeating students		210	82	85
Repeating students		43	81	80
Total students		253	82	83

[a] Question A: Do you feel that the program was successful in teaching you the principles of equilibrium?
[b] Question B: Would you voluntarily use other programs in general chemistry if they were available?

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Columbus

A Simple Model to Illustrate Conformational Effects in Acyclic Molecules

We have designed a simple model that is quite effective for demonstrating rotational forms about a carbon-carbon bond because of its excellent visibility in large classrooms.

Two 12-inch diameter circles are cut from 1/8-inch lucite. A 1/4-inch hole is bored in the center of each. Three strips of colored tape (Scotch Pressure Sensitive Tape, 3/4-inch width, 4-inches long) are applied to each Lucite circle, so that each radiates from the center hole at an angle of 120° to its neighbor (Fig. 1). Bright red strips are used on one disc and white on the other. This combination seems to provide the most striking and visible contrast. The two disks are fastened together about one in. apart with a machine bolt, washers, a spring, and a wing nut (Fig. 2).

Various functional groups are drawn on circles of filter paper, using a heavy marking pen. Various sizes of filter paper are used to give some indication of the relative sizes of the functional groups involved.

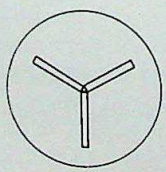


Fig. 1

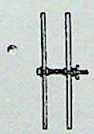


Fig. 2

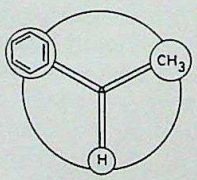


Fig. 3

The filter paper circles are then attached to the lucite disks with an easily removable adhesive (Fig. 3).

The same idea can be extended to overhead projection facilities by simply drawing in color three bonds, 120° apart, with functional groups at the ends, on each of 2 circles of stiff, transparent celluloid about 6 inches in diameter. The discs are fastened together by a paper fastener passed through their centers. They are placed on the glass plate of the projector and the top disc rotated to illustrate the various rotamers.

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Community Resources Pool
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Separation of Plant Pigments by Thin Layer Chromatography

The technique which is commonly used for separation of chloroplast pigments is based on the concept of chromatographic adsorption discovered by Tswett more than fifty years ago. The procedure consists of washing the chloroplast pigments down a column of powdered sugar with a mixture of polar and nonpolar solvents. The two chlorophylls, *a* and *b* are separated into two bands which are then isolated mechanically and transferred in solution for further study. Numerous papers (*1–5*, *7*) employing this technique have been published recently, giving the chlorophyll content of various green plant and vegetable leaves.

Paper chromatography, both the adsorption technique (*2*, *6*, *10*) and the partition method in which the paper is impregnated with organic solvents (*11*), have been employed in separation of plant pigments.

The purpose of this project was to attempt to separate chloroplast pigments over a thin layer of silicic acid. The original idea which was introduced by Kirchner (*9*) in 1951 was called chromatostrip and was used for separation of the constituents of citrus oils.

Employing this technique we are able to separate twelve distinct compounds on a rather short strip. The whole operation is carried in a test tube. Chlorophylls separated on a sugar column invariably contain other pigments when rerun on a silicic acid strip.

The Experiment

Preparation of Silicic Acid Strips. Provided suitable chromatographic tanks are available, any size glass strip may be employed. Our work is conducted on a 1 × 8-in. strip which fits a 10-in. test tube (Fig. 1).

Two hundred ml of a solution of 2.5% wheat starch powder in water is heated on a water bath to about 70°C and then set aside to cool slowly to room temperature. To this 95 grams of silicic acid (100 mesh powder, analytical grade) is added. The mixture is blended thoroughly in a blender. Enough water is added (usually it requires another 50 ml water) while blending to bring it to a pourable state. This mixture is then poured over glass strips and smoothed out mechanically by a wet-film adjustable applicator to a thickness of 1-mm. Six 1-in. wide strips can be handled at one time. Air bubbles which cause blisters to the surface film on drying are avoided.

It takes about twenty minutes for silicic acid to set. The strips are then put in an oven at 80° C for one hour. The oven temperature is raised to 110°C and the strips are heated at this temperature for two hours. Then they are removed from the oven and kept in a desiccator.

Extraction of Pigments from Green Leaves. Green leaves are homogenized in a blender with enough 50% methyl alcohol to just cover the leaves. The mixture is centrifuged and the upper liquid layer containing practically no pigment is poured out. The green solids are mixed with equal weight of filter aid (diatomaceous earth) and packed loosely into a short column. The pigments are washed out with acetone, and then transferred to a small volume of petroleum ether in a separatory funnel with the aid of excess water. The ether solution of the pigments is dried by passing it through a column of sodium sulfate and then concentrated with the aid of a stream of nitrogen. The concentrated pigments are kept at −15°C.

Equipment. The wet film applicator with adjustable micrometer was purchased from Gardner Laboratories, Inc. Visible spectrum of isolated chlorophylls and pheophytins was run by Perkin-Elmer Automatic Spectracord.

Development of Pigments. Practically all our work is based on ascending type chromatography. The concentrated pigments are spotted by means of a micropipet or a capillary about 1.5 cm from the long edge of the strip and immediately introduced into the test tube containing 5 to 10 ml of developer. The liquid front usually reaches the top of the strip before the pigments are separated into distinct spots without overlapping. In order to keep the liquid in a dynamic upward movement, a piece of filter paper wick is adjusted with one end touching the top layer of silicic acid film and the other folded over the rim of the test tube exposed to the air outside. The test tube is purged with nitrogen,

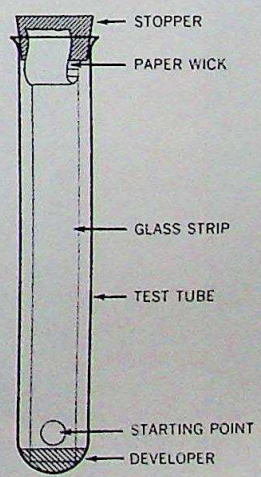


Figure 1. Chromatographic accessories.

[1] Address reprint requests to Dr. Anwar at 40 Hickory Hill Road, Tappan, New York.

[2] Peter Laplaca, Stephen Norman, Bruce Anwar, Lloyd Dutton, Ann Chamberlain, Beatrice Hsia, Beth Bloom, and Dodd Pullman are the students who contributed especially to this project.

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Table 1. Summary of Tests and Observations.

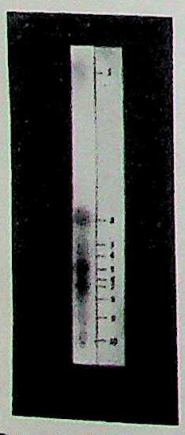
Spots no.	Identification	Visible color	UV (long) color	Adsorption peaks (mμ) Major	Minor
1	Carotenes	yellow	...	661, 406	605, 557, 530, 502
2	Pheophytin *a*	dark grey	orange-red	653, 432, 412	600, 530, 520
3	Pheophytin *b*	lt. grey	orange-red	659, 407, 425	607, 531, 502
4	Chlorophyll a^1	blue	orange-red	655, 410, 422	610, 570, 530, 502
5	Chlorophyll *a*	blue	orange-red	637, 448, 425	605, 530, 502
6	Chlorophyll b^1	green	orange-red	639, 450, 432	605, 590
7	Chlorophyll *b*	green	...	...	...
8	Xanthophyll	yellow	...	...	...
9	Xanthophyll	yellow	...	...	...
10	Xanthophyll	yellow	...	...	...
11	Xanthophyll	yellow	...	...	...
12	Xanthophyll	yellow	...	...	...

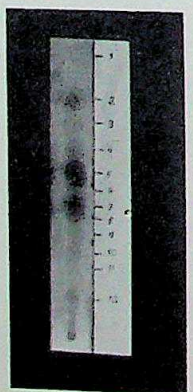
stoppered, and placed at the desired temperature in the dark for development of pigments. Liquid entering the paper, evaporates as it reaches the air outside the test tube, causing more liquid to enter the paper Fig. 1.

Results and Discussion

In our attempt to separate chloroplast pigments present in green leaves, numerous methods of pigment extraction and various developing solvent combinations were tried under different conditions of temperature. We find that by eliminating most of the water from the system initially with the aid of methyl alcohol and a centrifuge and by extracting the pigments from a column in the dark at low temperature and under inert atmosphere, the extraction is completed with a minimum of time and oxidation changes.

Studying various developing solvents, we find that a combination of polar and nonpolar is necessary for a good separation of plant pigments. An entirely nonpolar solvent has no effect on pheophytins, chlorophylls or xanthophylls. Alcohols exert the greatest effect, followed by ketones and ethers in that order. However, alcohols even in small percentages seem to collect all the pheophytins and chlorophylls together. Ethers are poor developers as such, but exert some beneficial effect on ketones. Chlorinated hydrocarbons behave somewhat like ethers. Developers containing 60% isooctane, 20% acetone and modified by 20% ether, or carbon tetrachloride, prove to be excellent developing solvents. The sequence of spots for pigmented compounds in spinach for these two developing solvents are seen in Figures 2 and 3, respectively.





Left, Figure 2. Chromatogram of spinach pigments. Developer: isooctane—60%, acetone—20%, ether—20%. Right, Figure 3. Chromatogram of spinach pigments. Developer: isooctane—60%, acetone —20%, carbon tetrachloride—20%.

The spot colors which are clear and bright at the end of the development period fade, and change color fairly rapidly on exposure to light and air. However, their freshness can be preserved for some time if the strip is covered with a layer of glycerine.

For identification purposes, each color spot zone along with silicic acid is scratched out into a small test tube containing a few mls of a polar solvent such as acetone. The dissolved color is clarified by passing it through a tiny cotton plug attached to a microfunnel or glass tubing.

No quantitative estimation of various pigmented compounds has been attempted by us so far. However, visual observations indicate that chlorophyll *a*, in fresh leaves exists in largest amount followed by chlorophylls *b*, a^1 and b^1. There is a close relationship between chlorophylls *a* and a^1 on one hand and *b* and b^1 on the other. In each pair their major adsorption peaks fall very close on the long wavelength side and only minor differences are observed between each pair on the short wavelength side of the visible spectrum. Besides that, the R_f's. of each pair are extremely close on the silicic acid strip. Probably each pair is the isomeric form of each other.

These two minor chlorophylls are probably the ones designated by Strain (*12*) as chlorophyll a^1 and b^1. Jeffrey (*8*) also noticed two minor chlorophylls separating from the main spots of chlorophylls *a* and *b*, especially in older extracts. The pheophytins *a* and *b* are shifted somewhat to the longer wavelength of their chlorophylls. All spectra are run in isooctane.

In aged or badly bruised leaves there is a drop in chlorophyll *a* content and a corresponding increase in allomerized chlorophylls and possibly pheophytin *a*. Usually the concentration of pheophytin *b* is exceedingly small. Allomerized chlorophylls are so strongly adsorbed by silicic acid that they hardly move.

Since chlorophylls are extremely susceptible to chemical, enzymatic, and photochemical changes, strict precaution is taken to minimize these factors. The extraction and concentration of pigments are performed in about an hour, most of it in the dark at low temperature. Separations are carried in the dark under nitrogen atmosphere. A complete chromatogram at room temperature requires 2 to 3 hours and at −15°C about 8 to 16 hours.

Acknowledgment

We are deeply indebted to the Community Resources Pool of the Rockland. Foundation and the South Orangetown Central School District No. 1, and to the

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school administrators and teachers of the Tappan Zee High School for making the realization of this project possible. The paper submitted as a result of this project represents the cooperative effort of all the students in the chemistry seminar. In addition to the two-hour seminar on Saturday mornings, these students have also worked many hours on this project in the basement of the author's home.

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Thin Layer Chromatography Apparatus

A simple and inexpensive apparatus for thin layer chromatography (TLC) has been developed which can be assembled from commonly available laboratory glassware and chemicals, and which obviates the applicators and supporting templates usually used. The technique should be of value in the student laboratory as well as being satisfactory for routine use. It consists of glass plates cut into two convenient sizes: 20 × 20 cm and 5 × 20 cm (which are grooved in order to contain the adsorbent layer), a glass developing chamber[2] large enough to accommodate the larger plates, and a 1-liter graduated cylinder cut off at the 600-ml mark which serves as a developing chamber for the smaller plates. A desiccator is unnecessary if the adsorbent layer is to be of cellulose or its derivatives, but for layers which require storage in a dry atmosphere (e.g., activated silica gel or alumina), a large desiccator can be constructed from a 12- × 12-in. Pyrex cylindrical jar with cover and fitted with a No. 5 porcelain desiccator plate and small Petri dishes for the desiccant.

Preparation of the Grooved Plate

The grooved plates are formed by masking the areas which will later contain the adsorbent with 1/2-in. wide plastic electrical tape spaced about 1/8 in. apart and then coating the entire plate, front and back, with Glyptal varnish.[3] After the resin coat has dried, the tape is stripped off and the plate is immersed in an etching bath containing 114 g of ammonium bifluoride per liter of water. A polyethylene dishpan serves as an inert tray, and the solution is stored in a polyethylene container which can be kept tightly closed. After approximately 7 1/2 hr at room temperature, during which the solution is gently agitated by a polyethylene-coated mechanical stirrer, the plate is removed, rinsed with hot water and then with acetone to remove the Glyptal, and finally cleaned in dichromate cleaning solution followed by thorough rinsing with distilled water. The depth of the grooves (which is quite uniform) is about 0.3 mm, depending on the type of glass used, and can be varied according to the duration of immersion; this should be determined on small trial pieces of the glass to be used.

Preparation of Adsorbent Layer

Slurries of the various adsorbents are prepared according to usual TLC techniques.[4] A cellulose layer for a 20- × 20-cm plate (which can contain about 12 channels) is prepared by vigorously stirring 3.5 g of cellulose powder[5] with 18 ml of acetone in a 50-ml Erlenmeyer flask. A magnetic bar works very well for this purpose. The slurry is poured evenly across one end of the grooved plate, then spread with a straight edge (glass plate) across the remainder of the plate in the direction of the grooves. After drying, the ridges between the grooves are scraped free of adsorbent and the plate is ready for use. If only two or three compounds are to be chromatographed, a 5- × 20-cm plate is prepared using 1 g of cellulose and 5 ml of acetone.

Acknowledgment

Appreciation is expressed to Dr. W. H. Langham of this laboratory for his encouragement and assistance and to Prof. Dr. F. Cramer, T. H. Darmstadt, Germany, for suggesting the use of grooved glass which is commercially available (as a building material) in Europe.

[1] Work performed under the auspices of the U.S. Atomic Energy Commission.

[2] Developing tanks large enough for the 20 × 20-cm plates are commercially available from Brinkmann Instruments, Inc., 115 Cutter Mill Road, Great Neck, N. Y., and No. 6944 from Corning Glass Works, Corning, N. Y.

[3] General Electric Glyptal varnish, No. 1202.

[4] Randerath, K., *Biochem. Biophys. Res. Comm.*, 6, 452 (1962); Randerath, K., and Struck, H., *J. Chromatog.*, 6, 365 (1961); Wollish, E. G., Schmall, M., and Hawrylyshyn, M., *Anal. Chem.*, 9, 1139 (1961); Hofmann, A. F., *Anal. Biochem.*, 3, 145 (1962).

[5] Adsorbents for TLC, average particle size <10 μ, are available from Macherey, Nagel and Co., Düren, Germany; distributed by Brinkmann Instruments, Inc.

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Thin Layer Chromatographic Separation of Leaf Pigments

A rapid demonstration

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Eleven pigment spots can be detected from an extract of grass leaves by a rapid thin layer chromatography (TLC) separation on silicic acid. The technique is simple and makes an interesting demonstration or student experiment.

Preparation of pigments. Crush green leaves in a mortar with a few milliliters of alcohol or acetone and twice this volume of petroleum ether. Transfer the solution to a separatory funnel and swirl with an equal volume of water. Allow the phases to separate and discard the lower water phase. Repeat the water washing twice. Decant the petroleum ether phase to a bottle and add two grams of anhydrous sodium sulfate. If the pigment solution is too weak, it can be concentrated by evaporation with a stream of dry nitrogen.

Procedure. To 5-g Biosil A-30B[1] in a beaker add 12-ml water and stir vigorously for 15 sec or until thoroughly dispersed. Pour about one milliliter of this mixture onto a clean microscope slide. Spread the slurry with the stirring rod and tap the slide gently to settle the silicic acid in an even film. Allow to set for a couple of minutes then activate by drying in an oven at 110°C for 15 min or longer.

When the dried slide has cooled to room temperature, place one drop of the leaf pigment extract 1.5 cm from one end. Place the slide vertically with the spot end down in a 250-ml beaker containing a 1-cm layer of benzene:acetone, 7:3 v/v. Cover with a watch glass.

The solvent rapidly rises through the thin layer of silicic acid. Separation of the pigments is apparent almost immediately. Carotenes move the most rapidly followed by chlorophyll *a*, chlorophyll *b*, and xanthophylls. Eight spots are readily detected and two or three additional spots with more difficulty.

Alternatively, the slide may be air-dried overnight. This produces a silicic acid layer of lower adsorptivity. Also, lower percentages of acetone may be used for better separation of chlorophyll *a* and *b*. An alternate procedure is the use of benzene: acetone, 95:5 v/v, and continued development for one-half hour with the cover glass removed from the beaker.

[1] TLC Silicic Acid is available from Bio-Rad Laboratories, 32nd and Grillin, Richmond, California.

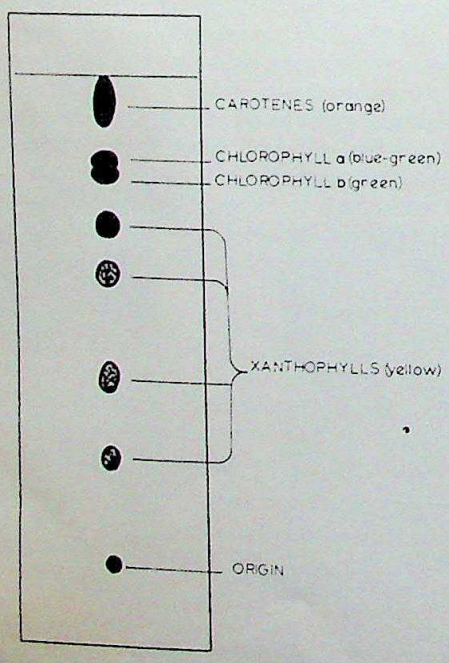


Figure 1. Tracing from TLC separation of green leaf pigments.

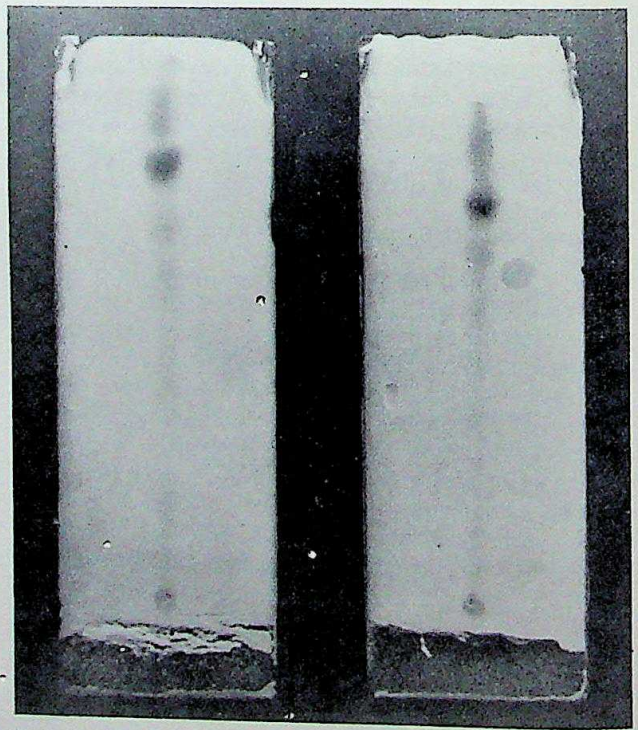


Figure 2. Photograph of TLC separation of the same green leaf pigments on different slides.

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A radiochemistry experiment

Extraction of Cobalt(II) Complexes

The extraction of chloro-complexes of cobalt(II) with long chain tertiary amines illustrates to students the use of tracer techniques as applied to distribution measurements[2] and provides insight into the behavior of the chloro-complexes of cobalt(II). The experiment logically involves a study of the dependence of the distribution ratio upon hydrochloric acid concentration followed by a study of the effect of amine concentration. The former establishes the optimum hydrochloric acid concentration for the extraction of cobalt(II). The latter provides information concerning the determination of a convenient amine concentration for the efficient extraction of cobalt(II) and an indication of the cobalt(II) species found in the organic phase. About 6 hrs. are required for a student to perform the necessary laboratory work.

The experiment begins with the preparation of a 10% by volume solution of trilaurylamine[3] in xylene. This amine solution is equilibrated with 6 *M* hydrochloric acid so that no net hydrochloric acid transfer will take place during the extraction operations. Small volumes of the resulting amine hydrochloride solution are subsequently equilibrated with equal volumes of 1 to 12 *M* HCl solutions each containing about 10^4 c/m of cobalt-60 tracer. After separation of the two phases by centrifugation a sample of each phase is transferred to counting tubes by means of transfer pipets and the relative activity measured in a well-type scintillation counter. The success of the experiment is in jeopardy at this point unless the student takes special care not to contaminate the aqueous phase with the tracer-rich organic phase. The distribution ratio is obtained by dividing the c/m/ml of the organic phase by the c/m/ml of the aqueous phase. Typical student data for this experiment is illustrated in Figure 1. There is a maximum in the distribution ratio at about 8 *M* HCl.

For the determination of the distribution ratio dependence on the amine concentration, the 10% trilaurylamine solution is diluted with xylene to make several solutions having trilaurylamine concentrations ranging from 0.1 to 5%. These solutions are then equilibrated with cobalt-60, hydrochloric acid solutions and the distribution ratio determined as described above. The hydrochloric acid concentration is 6 *M* in order to reduce the problem of contamination of the aqueous phase by the tracer rich organic phase while still keeping conveniently measurable distribution ratios at low amine concentrations.

Under conditions of low amine concentrations the distribution ratio, D, should obey a limiting expression,

$$D = Q' (\text{Amine})^n$$

with deviations expected at higher amine concentrations due to the formation of new complexes. Q' is a

[1] Present address, Hanford Laboratories, General Electric Co., Richland, Washington.

[2] See for example: Mahlman, H. A., Leddicotte, G. W., and Moore, F. L., *Anal. Chem.*, 26, 1939 (1954).

[3] Trilaurylamine may be obtained from Archer Daniels Midland, 700 Investors Building, Minneapolis, Minnesota.

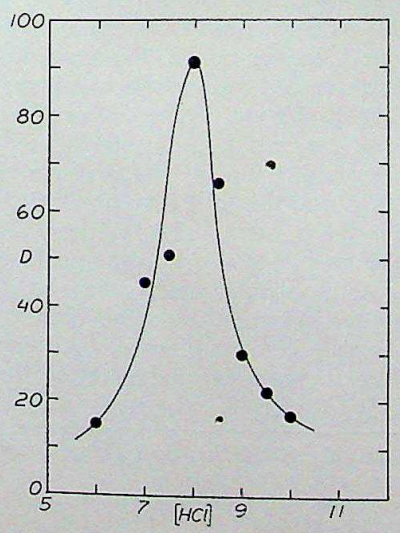


Figure 1. A plot of the distribution ratio (c/m/ml of cobalt-60 in the amine-xylene phase divided by the c/m/ml of cobalt-60 in the hydrochloric acid phase) as a function of hydrochloric acid concentration. The extracting solvent was 10% v/v trilaurylamine in xylene, and the hydrochloric acid concentrations are expressed in moles/liter.

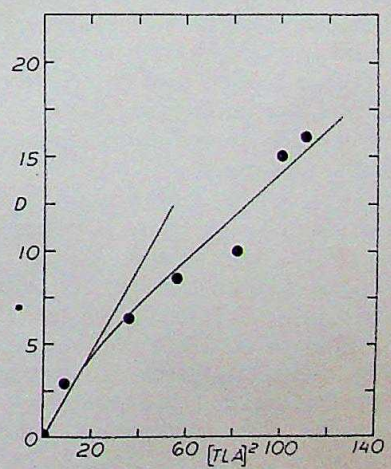


Figure 2. A plot of the distribution ratio against the square of the amine concentration, showing the deviation from the second power dependence at higher amine concentrations. The hydrochloric acid concentration was 6M.

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formal equilibrium constant for extraction of cobalt(II) from a particular concentration of hydrochloric acid. Plots of the distribution ratio versus various powers of the amine concentration may be used to determine the value of n. Alternately, n may be determined from the slope of the line when the log of the distribution ratio is plotted versus the log of the amine concentration. Figure 2 is a typical student plot of the distribution ratio against the square of the amine concentration and shows the deviation from this relationship at higher amine concentrations. Once the amine concentration dependence, n, is found, Q' may be calculated.

The student should explain the significance of the maximum value observed in the plot of the distribution ratio versus the hydrochloric acid concentration. The student should also determine the composition of the cobalt(II) species present in the organic phase. If, for example, the plot shows that there is a second power amine dependence, as our students have found, it then suggests that the cobalt(II) species in the organic phase may be $CoCl_4(Ham)_2$. Recent work of Good and Bryan[4] have confirmed this assumption.

Suggested variations to the above procedure are the extraction of cobalt(II) from solutions of thiocyanate, oxalate, and other complexing anions. Other amines such as tri-n-octylamine, triisooctylamine, and tri-n-decylamine can also be used.

[4] Good, M. L., and Bryan, S. E., *J. Inorg. and Nuclear Chem.*, **20**, 140 (1961).

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A radiochemistry experiment

The Solubility of Thallium(I) Bromide

There are several reasons why the study of TlBr solubility is particularly adaptable to student experimentation. The 0.77 Mev beta emitted by thallium-204 is easily counted by standard end-window Geiger-Müller counters. The solubility of thallium(I) bromide in water is such that 5 microcuries of thallium-204 and 15 mg of thallium(I) nitrate are sufficient to obtain convenient and accurate counting rates with 0.1 ml assays of the supernatant solution. Fifty microcuries of thallium-204, which can be obtained without exceeding the general AEC license, is sufficient tracer for a class of about ten students. The experiment is completed with little difficulty in a 3-hr laboratory period and demonstrates the concept of specific activity and its application to the determination of a slightly soluble salt.

The students first determine the activity of the thallium-204 tracer solution by evaporating an aliquot of the tracer on a planchet and counting it with an end-window Geiger-Müller counter. If the tracer is not thallium(I), a few milligrams of sulfite should be added to the solution to reduce thallium(III) before the experiment is performed.

While evaporating the tracer assay, the student carefully weighs out 15 mg of dry thallium(I) nitrate and dissolves it in a few milliliters of water. About 5 microcuries of the assayed thallium-204 tracer is then carefully pipetted into the thallium(I) nitrate solution, and a few milliliters of 0.1 M sodium bromide are added. Under these conditions the tracer is almost completely precipitated but the student should check this by assaying the supernatant solution. The thallium(I) bromide precipitate is washed with 0.01 M sodium bromide, centrifuged, and the supernatant solution discarded. Ten milliliters of water is added to the centrifuge tube which is then heated to about 80°C for a few minutes to dissolve some of the precipitate.

The centrifuge tube containing the precipitate is placed in a constant temperature bath at 25°C and equilibrium is approached by the reprecipitation of the dissolved thallium(I) bromide. After 30 min the centrifuge tube is removed from the bath, centrifuged, and an aliquot of the supernatant solution removed and evaporated on a planchet under a heat lamp. This assay is then counted to determine the thallium-204 content of the solution. The sampling is repeated at 30-min intervals to determine whether or not equilibrium has been attained. Generally, equilibrium is reached in about an hour and a half.

In order to determine the solubility of thallium(I) bromide, the student must first calculate the specific activity from a knowledge of the quantity of tracer added to the weighed amount of thallium(I) nitrate. The solubility of this salt is then determined from the activity of the supernatant solution. The solubility of thallium(I) bromide found by our students ranged from 0.4 to 0.5 g/ml, and the solubility product ranged from 2.8×10^{-6} to 3.8×10^{-6}. (Lit. value = 3.6×10^{-6}.[2])

The solubility as a function of bromide ion concentration and ionic strength may also be determined. In this way the common ion effect and complex ion formation[3, 4] can be investigated. A demonstration experiment of the common ion effect on the solubility of thallium(I) chloride[5] has been described.

[1] Present address; Hanford Laboratories, General Electric Co., Richland, Washington.

[2] Latimer, W. M., "Oxidation Potentials," 2nd ed., Prentice-Hall, Inc., New York, 1952, p. 164.

[3] See for example: Hu, K. H., and Scott, A. B., *J. Am. Chem. Soc.*, **77**, 1380 (1955).

[4] Scott, A. B., Dartau, R., and Sapsoonthorn, S., Abstracts, Northwestern Regional Meeting, American Chemical Society, June 16, 17 (1960).

[5] Roig, E., Riekehoff, I. G., Russo, C. S., Curet, J. D., J. Chem. Educ., **38**, 350 (1961).

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A radiochemistry experiment

Some Chemical Properties of Neptunium

The purpose of this undergraduate-level radiochemistry experiment is to examine the chemistry of neptunium. Part of the experiment repeats classical chemical studies of Seaborg and Wahl (*1*), and part of the experiment involves the study of ion exchange and solvent extraction techniques currently used to isolate neptunium. By doing such experiments with neptunium-239 the chemistry of an actinide element can be obtained without the hazard associated with an alpha emitter. Through additional reading (*2*, *3*) and classroom discussion the student can learn about the analogous chemistry of the other actinides.

Neptunium-239 is conveniently produced by neutron irradiation of uranium-238. To emphasize the nuclear transformations involved in the production, the student should calculate the amount of neptunium formed during the irradiation from the weight of uranium, the neutron flux, and the irradiation time. A microcurie of neptunium-239 is quite sufficient for each student. Since it is desirable to allow the short-lived fission products to decay for one or two days before permitting students to begin the experiment, it is not necessary to have a reactor in the immediate locality, provided that convenient shipping arrangements can be made.

The irradiated uranium is dissolved in a few milliliters of 4 *M* nitric acid-0.01 *M* iron(II) chloride-0.02 *M* sulfamic acid solution. Hexanitrato neptunium(IV) ion is separated by either absorption on a Dowex-1 column and elution with 0.25 *M* nitric acid (*4*, *5*) or by extraction with an equal volume of 10% (v/v) trilaurylamine in xylene (*6*). The neptunium-239 is removed from the trilaurylamine solution by equilibration with 2 ml of 5 *M* perchloric acid. The extraction procedure is faster and easier for the student although excellent fission product decontamination is obtained by either method. The student confirms the radiochemical purity by following the decay of a separated sample for two weeks.

After the neptunium-239 has been separated, 10^4 c/m aliquots are treated with Fe^{2+}, MnO_4^{1-}, $Cr_2O_7^{2-}$, and Ce^{4+} in order to selectively form neptunium(IV) or neptunium(VI). Each oxidation state is then treated with 10 mg of lanthanum and 1 ml of hydrofluoric acid, and the amount of coprecipitation determined by counting the precipitate. The amount of coprecipitation with bismuth phosphate is determined in a similar manner. To reduce contamination problems and to avoid filtering and mounting, the separated precipitates may be slurried into counting tubes and counted in a well-type scintillation counter. This procedure speeds up the experiment considerably. By judicious selection of additional oxidizing and reducing buffers (*1*) and noting which oxidation state is coprecipitated, the formal neptunium(IV)-neptunium(VI) potential may also be obtained as an optional part of the experiment.

The distributions of neptunium(IV) and neptunium(VI) between carbon tetrachloride solutions of tributyl phosphate and nitric acid and between hexane and nitric acid are studied next (*7*). These experiments are conveniently done on a milliliter scale with stoppered centrifuge tubes and a little shaking. Additional studies involve the determination of the distribution ratio as a function of the nitric acid concentration. Also the study of the extraction of neptunium(IV) with methyl isobutyl ketone or with xylene solutions of some tertiary amine, such as tri-*n*-octylamine, can be carried out.

The time required for this experiment depends upon the number of precipitations and distributions done, but usually two three-hour laboratory periods are sufficient. Additional time is required for the determination of the half-life of neptunium-239.

[1] Present address, Hanford Laboratories, General Electric Co., Richland, Washington.

Literature Cited

(1) Seaborg, G. T., and Wahl, A. C., "The Transuranium Elements," edited by Seaborg, G. T., and Manning, W. M., McGraw-Hill, New York, 1949, paper 1.6, p. 25.
(2) Katz, J. J., and Seaborg, G. T., "The Chemistry of the Actinide Elements," John Wiley and Sons, New York, 1957.
(3) Hindman, J. C., J. Chem. Educ., **36**, 21 (1959).
(4) Ryan, J. L., U. S. Atomic Energy Commission document, HW-59193, Sept., 1959.
(5) Sheppard, J. C., and Becker, G. V., unpublished documents.
(6) Keder, W. E., Sheppard, J. C., and Wilson, A. S., *J. Inorg. and Nucl. Chem.*, **12**, 327) (1960).
(7) Seaborg, G. T., and Wahl, A. C., *ibid.*, pp. 252–8.

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Collected by
Alfred B. Garrett
Ohio State University
Columbus

The Flash of Genius, 12

Radioactive Tracers: George de Hevesy

A failure in a laboratory project—a failure to separate radium-D from lead—started George de Hevesy on a long productive series of researches on radioactive tracers. This was the road to the use of radium D, now known to be the radioactive isotope ^{210}Pb, as a "tracer" in reactions involving lead.

Dr. Hevesy is credited with being the first to apply both natural and artificial isotopes as tracers in studies of plants and animals. He pioneered in the use of radioactive tracer techniques in chemistry, biology, and medicine. For this work he received the Nobel Prize in 1943 and the Atoms for Peace Award in 1959. Dr. Hevesy tells his story as follows:[1]

"Ernest (later Lord) Rutherford, then in Manchester, simultaneously with the discovery of the nucleus of the atom and the study of its properties, was interested in other investigations. Among those investigations was a study of the velocity and absorption of β-particles. Radium D emits very soft β-rays, and the investigation of the properties of the latter required a strong preparation of the radioactive material. Rutherford's institute had appreciable amounts of radium D at their disposal; however, it was mixed with large amounts of lead. A few hundred kilograms of lead chloride containing appreciable amounts of radium D obtained from pitchblend were presented to Rutherford by the Austrian Government which at that time, owned the only uranium mine—Joachimsthal in Bohemia.

"The lead chloride was stored in the cellar of the institute. One day when I met Rutherford in the cellar, he suggested that if I were worth my salt, I should separate radium D from all that nuisance of lead. Being a young man, I was an optimist and fully convinced that I would succeed; but even though I worked very hard for a year, trying a large number of separations, I failed entirely. To make the best of this depressing situation, I decided to make use of the inseparability of radium D from lead. By adding pure radium D of known activity to 1 mg of lead nitrate, the lead present in that compound could be labeled, and its path followed through chemical reactions with the aid of radioactive measurements.

"In 1912, I was spending Christmas at my parent's home in Budapest. I wrote to Dr. Paneth, then an assistant at the Vienna Institute of Radium Research, whom I had met a few weeks earlier when visiting there. I proposed to him that we jointly determine the solubility of sparingly soluble lead sulfides and lead chromates by labeling them with radium D which was available in large amounts and pure condition at the Vienna Institute. The radon formed by decay of radium was pumped off each week, the radium D in turn was available as a decay product of this radon.

"We started our joint investigations with Paneth early in January, 1913, followed by other applications of labeled lead and labeled bismuth in problems of inorganic and electrochemistry. Our first paper was published in 1913 in *Zeitschrift für anorganische Chemie*.[2]

"In the following decade radioactive indicators found application only in the field of inorganic and physical chemistry. Only lead, bismuth, radium, actinium, and thorium could be labeled.

"In 1923, while engaged in the study of the properties on the newly discovered element hafnium at Niels Bohr's Institute in Copenhagen, I got interested in problems of batanica and studied the transportation of lead in bean seedlings using thorium B labeled lead salts. The results of these investigations were published in the *Biochemical Journal* in 1923.[3]

"Dermatologists were interested in those days in replacing arsenic by bismuth in the therapy of syphilis, and my friend the dermatologist Lomholt asked me to advise him in the study of the distribution of bismuth in the animal organism. I suggested using radium E labeled bismuth. The results of investigations of the distribution of labeled bismuth and labeled lead in the rabbit carried out by Christiansen, Lomholt and myself were published in the *Proceedings of the Paris Academy of Sciences* in 1924.

"In April, 1913, after terminating our investigations with Paneth in Vienna, I was indulging in a cup of tea in the Rutherford Institute in the company of Moseley, the founder of X-ray spectroscopy. I happened to mention that I would be much interested in following the path of water molecules contained in the cup of tea through my body. Moseley, a man of great vision, considered my wish to be much too exacting. However, before two decades elapsed, Urey's discovery of heavy water made it possible to label water and to follow the path of labeled water.

"Shortly after his discovery Urey most kindly supplied me with a few liters of labeled water. His water contained $^1/_2$ p.c. of heavy water, which however sufficed to study the interchange of water molecules of the goldfish and those of the surrounding water and to determine the water content of the human body and the mean life time of the water molecules of the latter.

"The availability of concentrated heavy hydrogen made possible the demonstration of the dynamic nature of numerous body constituents by Schonheimer and Rittenberg. These workers applied another stable tracer ^{13}N in their most important studies. Concentrated ^{15}N, ^{13}C, and ^{18}O became available through Urey's work.

"The above mentioned stable isotopes appreciably

[1] Hevesy, G., Personal Communication.

[2] Hevesy, G., *Zeit. fur Anorg. Chem.*, 82, 223–8, 1913.

[3] Hevesy, G., *Biochemical Journal*, 17, 439–45 (1923).

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increased the number of tracers. The greatest progress was, however, due to the availability of radioactive isotopes of almost every element following the discovery of artificial radioactivity by Frédéric and Iréne Curie Joliot. Shortly after this discovery we applied radioactive phosphorus prepared by irradiating 10 liters of carbon disulfide with neutrons emitted by mixtures of radium and beryllium. In the first study it was demonstrated that about 1/3 of the mineral constituents of the skeleton is constantly renewed. This investigation was followed by the study of renewal rate of phosphatides and carbohydrates and the formation rate of desoxyribonucleic acid and how this formation is influenced by irradiation with Roentgen rays using radioactive phosphorus as a tracer.

"While many of these studies could be carried out with radioactive phosphorus of very modest activity that could be produced by the action of our neutron sources on carbon disulfide—these sources were sufficient for our clinical blood volume measurements, when trying to trace the origin of the constituents of milk, this was no longer the case. In the experiments, goats were to be injected with radioactive phosphorus (made available through the generosity of Ernest Lawrence). The availability of the cyclotron-produced radioactive bodies was an immense advance in the application of tracers. Our tracers were prepared by Martin Kamen and mailed to us in airmail letters. Today such a procedure would not be permissible, but the mailed samples did hardly any harm to humans, and presumably, not even to simultaneously traveling photographic film."

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Constant Current Power Supply

A recent publication[1] in THIS JOURNAL concerns a constant current power supply for moving boundary transport number experiments. We wish to call readers' attention to another circuit which we have used several years for the same purpose and which we believe is superior. The circuit diagram shown in the drawing is a slight refinement of one developed by Winkel and Svec.[2] The following points should be noted:

1. The circuit in the drawing has a chassis ground on one of the output terminals for safety.

2. The regulation is more complete. Over the range 0.1 to 5 ma a current regulation of better than 0.1% can be expected. The regulation over the range 2–3 ma is 0.05% or better.

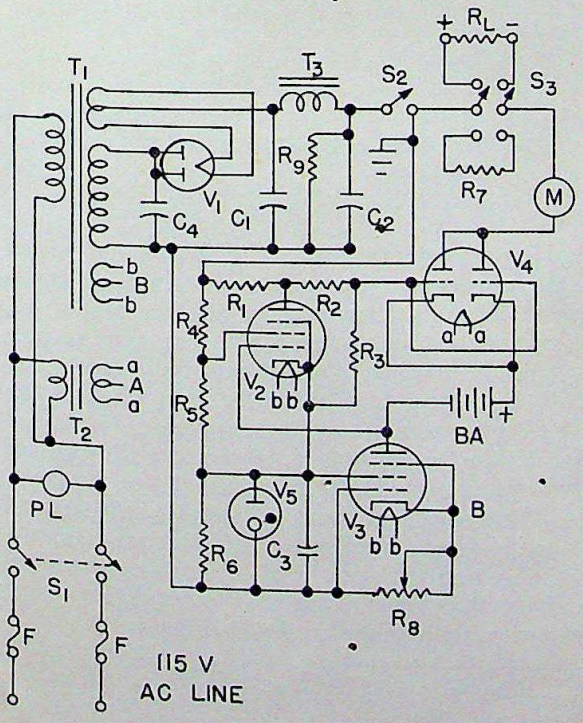
3. The complexity and cost of the power supply is not very different from that given in footnote 1.

4. The power supply described here takes advantage of both electronic amplification of any error signal in a feedback loop and the plate current characteristic of the pentode.

5. The battery in the circuit need be replaced only once a year. Probably a Zener diode such as the International Rectifier type 1Z12 can be substituted for the battery eliminating the need for battery replacement.

6. The meter indicates with the external circuit disconnected. The current is adjusted with the internal load connected.

[1] TOBEY, S. W., J. CHEM. EDUC., **38**, 517 (1961).
[2] WINKEL, D. E., AND SVEC, H. J., U.S.A.E.C. Declassified Report I.SC409 (1953).



Parts List

BA 12 V Battery
C_1, C_2 10 mf, 1000V
C_3 0.01 mf, 400V
C_4 0.85 mf, 1000V (Furnished with T1)
F Fuse, 2 amp.
M Meter, 0–5 ma.
PL Pilot Lamp, NE 51
R_1 150 K, 2 Watt
R_2, R_3 1 meg, 1/2 Watt
R_4 35 K, 10 Watt
R_5 10 K, 10 Watt
R_6 100 K, 1 Watt
R_7 47 K, 1 Watt (internal load)
R_8 5 K, log taper, Mallory 5 M 1
R_9 20 K, 50 Watt
R_L Load Resistance, transference Cell
S_1 DPST
S_2 SPST Plate Voltage switch
S_3 DPDT Shorting, Mallory type 3122J
T_1 Plate and filament voltage transformer, Sola type CVE 7106, 770 VCT, 110 ma; 5 V, 2a; 6.3V, 3a regulated voltages.
T_2 6.3V, 1a, Thordarson T21F08
T_3 10 henry, 110 ma, Stancor C1001
V_1 5Y3GT
V_2 6AG5 (Metal shield around tube)
V_3 5693 (6SJ7) (Shield connected to cathode)
V_4 5691 (6SL7)
V_5 OB2 (VR 105)

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A Unified Quantitative Interpretation of Two-Component Phase Diagrams

The quantitative treatment of phase diagrams in physical chemistry texts is usually confined to the use of the lever law in a discussion of a system containing a simple eutectic point (e.g., Bi-Cd). Students, exposed only to such elementary examples, usually experience trouble in the interpretation of diagrams containing congruently melting compounds and peritectics, particularly in cases where mole fraction is the composition variable. A large number of them, apparently following some mythical "law of conservation of moles," forget to correct the lever law calculations for the change in the number of moles accompanying compound formation. For the past several years, in an attempt to eliminate this common and persistent error, the author has used the approach described below in the introductory physical chemistry course.

This treatment involves the division of a diagram containing congruently melting compounds or peritectics into a series of simple eutectic systems by changing the original composition scale into several successive composition scales involving the compounds present. The number of scales required depends upon the number of compounds formed by the two-component system. Once the scale has been changed, the lever law applies directly, without the corrections for changes in the number of moles, just as in the case of systems which contain only simple eutectics and solid solutions. It should be noted that the ordinate in these diagrams can be any non-composition dependent variable such as temperature or pressure. The following discussion and example, based on Figure 1, will illustrate this approach.

This particular diagram is most conveniently separated into three simple eutectic systems: A-A_2B, A_2B-AB_3, and AB_3-B. The original A-B composition scale is thus divided into three successive composition scales in the order noted. The compositions of all eutectic mixtures and any other particular mixtures under consideration are then converted into compositions on the appropriate new scales. Diagrams containing peritectics are treated in exactly the same way.

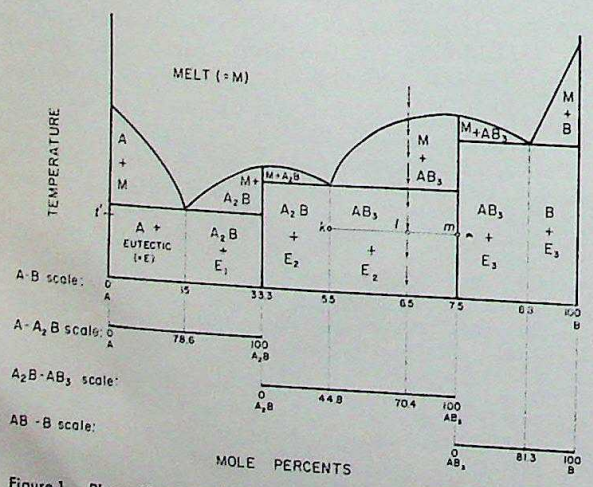


Figure 1. Phase diagram of the two component system A-B.

Example. Consider 100 moles of a molten mixture, initially 65 mole per cent B-35 mole per cent A, which is cooled to temperature t′. Determine the number of moles of each substance (i.e., AB_3 and A_2B) in the eutectic mixture at this temperature.

The compositions of the eutectic mixture containing AB_3 and A_2B (over-all composition 55B-45A) and the 65B-35A mixture are changed over to the A_2B-AB_3 scale by means of easy simultaneous equations based on the numbers of moles of A and B in each case:

x = moles AB_3, y = moles A_2B

Eutectic Mixture (55B-45A)	65B-35A *Mixture*
$3x + y = 55$	$3x + y = 65$
$x + 2y = 45$	$x + 2y = 35$
$x = 13$ AB_3, $y = 16$ A_2B	$x = 19$ AB_3, $y = 8$ A_2B
Total moles = $x + y = 29$	Total moles = $x + y = 27$
$\frac{13}{29} \times 100\% = 44.8$ mole % AB_3	$\frac{19}{27} \times 100\% = 70.4$ mole % AB_3

The lever law can now be applied directly to the 65B-35A mixture, using the A_2B-AB_3 scale:

$$\frac{\text{moles large crystals } AB_3}{\text{moles total}} = \frac{kl}{km}$$

$$\frac{70.4 - 44.8}{100 - 44.8} \times 27 \text{ moles} = 12.5 \text{ moles large } AB_3 \text{ crystals}$$

$$\frac{\text{moles eutectic mixture}}{\text{moles total}} = \frac{lm}{km}$$

$$\frac{100 - 70.4}{100 - 44.8} \times 27 \text{ moles} = 14.5 \text{ moles of eutectic mixture.}$$

14.5 moles × 44.8 mole % = 6.5 AB_3 in the eutectic.
14.5 moles × 55.2 mole % = 8.0 A_2B in the eutectic.

The other two eutectic mixtures in Figure 1 have been converted into compositions on the new scales by simultaneous equations similar to those of the example.

The nearest textbook approach to this type of presentation is a problem worked out for a peritectic system.[1] In that problem, however, the change in the number of moles accompanying compound formation is handled within the framework of the lever law rather than by means of initially changing the composition scales. The author has observed that students seem to be able to interpret complicated metallurgical diagrams more quickly and with fewer mistakes using the ideas noted above than by making all the corrections (and frequently forgetting some) in the lever law calculations.

[1] SHEEHAN, W. F., "Physical Chemistry," Allyn and Bacon, Boston, 1961, pp. 304–6.

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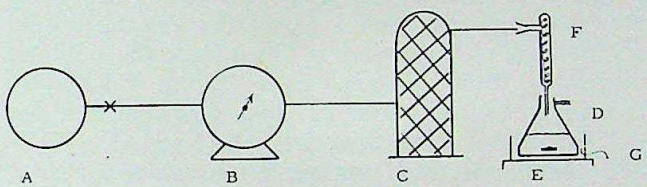
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A Convenient Synthetic Technique to Oxidize Mercaptans to Disulfides

Recently, we have studied the base catalyzed oxidation of mercaptans to disulfides in the presence of molecular oxygen.[1] In the initial stages of this work, it was necessary to have some type of accurate and simple technique that would enable oxygen consumption to be measured as a function of time at atmospheric pressure. The purpose of the present note is to report on this technique which appears to be useful as a synthetic tool in the oxidation of alkyl, aralkyl, and aromatic mercaptans to disulfides.

The atmospheric oxidation apparatus (see figure) consisted of a glass reaction vessel (*D*) and an oxygen source. The reaction vessel was a specially adapted heavy-walled 500-ml Erlenmeyer flask equipped with a side-arm 0.5 mm in diameter and 2 mm in length.



Oxidation apparatus: *A*, O_2 gas bag; *B*, wet test meter; *C*, drying tower; *D*, reactor; *E*, magnetic stirrer; *F*, water condenser; *G*, constant temperature bath.

Oxygen gas was supplied to the reaction vessel from a partially filled collapsible polyethylene gas balloon (*A*) of ca. 14-liter capacity through a wet-test gas meter (*B*), connected to a drying tower (*C*) packed with indicating Drierite, and finally through an overhead Friedrich's condenser (*F*) and into the reaction flask. The amount of oxygen initially admitted into the gas balloon had to be minimized so that the fluctuation of barometric pressure would not affect the readings on the gas meter. The reaction flask was thermostated within ± 0.5°C and stirred magnetically throughout.

In the actual utilization of this equipment 0.1 mole of the mercaptan was added to the reaction flask which contained the desired solvent-base system and a Teflon-covered stirring bar—in a nitrogen dry box. The reaction flask was sealed with a suitable ground glass cap, removed from the dry-box and attached to the oxidation apparatus which had been purged previously with nitrogen. The entire system was then purged with oxygen to displace the nitrogen through the reaction flask side-arm, the side-arm was sealed, and the wet-test meter was set to read zero when equilibrium pressure was estabilished. The reaction was then started by setting the Teflon-covered magnetic stirring bar in motion at 1100 rpm. The reaction was allowed to proceed until no appreciable oxygen consumption could be detected on the wet-test meter. The disulfides are obtained most conveniently by extraction with ether and then evaporating the ether extract. Further purification can be accomplished by distillation or recrystallization from alcohol depending on the physical state of the disulfide. Various types of mercaptans have been oxidized according to the above procedure in 100 ml solutions of 2 *M*. sodium methoxide in methanol or sodium hydroxide in water. Pertinent data are summarized in the table. Generally, good to excellent yields of each disulfide are obtained in both solvent systems. The methanol system is preferred however, since the reactions are usually complete in 2.5 to 11 hrs, depending on the mercaptan used. Under ordinary conditions, the reaction time in aqueous NaOH varies from 11.5 to 23 hrs to obtain comparable yields. If one uses one-quarter aliquots of the original reaction mixtures, this gives a useful, small scale preparative technique requiring about 1 to 3 hrs in methanol solution. Another alternative is to use trace amounts of an oxidation catalyst such as cobalt phthalocyanine (see table). In aqueous sodium hydroxide, e.g., a comparable yield of *n*-butyl disulfide is obtained in about one-eighth of the time interval (1.5 hrs) required for the non-catalyzed reaction.

The above technique has found wide use in a large number of atmospheric oxidation reactions studied in these laboratories. An additional advantage of this system is the fact that it can even be used at elevated temperatures. If volatile gases are evolved during the course of the reaction (e.g., CO_2) then the appropriate correction should be applied to the measured apparent rate of O_2 uptake. The apparatus could be also used at subatmospheric or superatmospheric pressures by placing the gas bag in a rigid enclosure equipped with a pressure gauge. In this modification, of course, the remainder of the equipment must be supplied with vacuum or pressure-proof parts. Thus, it should be of use to others who are engaged in similar work.

Oxidation of Various Mercaptans in Basic Media

Mercaptan	Solvent[a]	% Yield[c] of disulfide	Reaction time (hr.)
n-C_4H_9SH	Water	79	11.5
n-C_4H_9SH[b]	Water	61	1.5
sec-C_4H_9SH	Water	83	20.0
C_6H_5SH	Water	67	23.0
n-C_4H_9SH	Methanol	85	7.0
sec-C_4H_9SH	Methanol	77	11.0
$C_6H_5CH_2SH$	Methanol	84	2.5

[a] NaOH was employed as the base in water while NaOMe was employed in the methanol solvent.
[b] Cobalt phthalocyanine (100 mg) added as a catalyst.
[c] Based on the weight of disulfide after purification.

Presented in part at the 140th meeting of the American Chemical Society, Chicago, Illinois, September, 1961.

[1] Wallace, T. J. and Schriesheim, A., *J. Org. Chem.*, **27**, 1514 (1962).

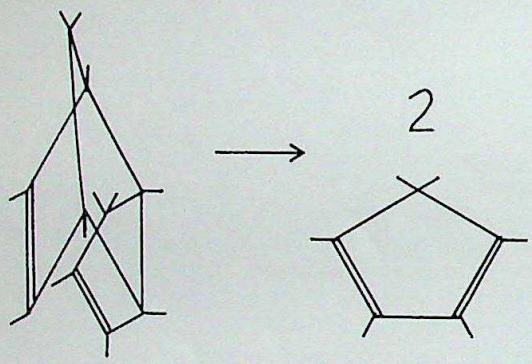
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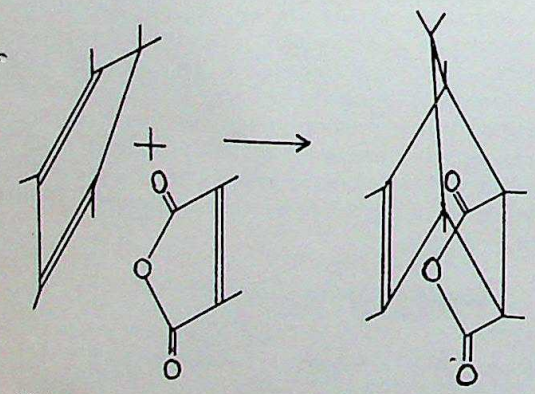
A Diels-Alder Reaction Experiment

Although some recent elementary organic chemistry laboratory texts include the Diels-Alder reaction,[1] we wanted one which would illustrate the reversible nature of the reaction and which could be completed in one afternoon laboratory session. With this in mind, the original method of Diels and Alder for the reaction of cyclopentadiene with maleic anhydride[2] was modified for use in the elementary organic laboratory. *Endo* Bicyclo[2,2,1]hept-5-ene-2,3-dicarboxylic anhydride is prepared by the Diels-Alder



"Dicyclopentadiene" Cyclopentadiene

reaction of cyclopentadiene with maleic anhydride in benzene, followed by recrystallization from mixed solvent. Cyclopentadiene is prepared from commercial dicyclopentadiene by reversal of the Diels-Alder reaction.



Cyclopentadiene
Maleic Anhydride

endo-Bicyclo[2.1.1]-hept - 5 - ene - 2,3-dicarboxylic anhydride

[1] For example, ROBERTSON, G. R., AND JACOBS, T. L., "Laboratory Practice of Organic Chemistry," 4th ed., Macmillan, New York, 1962, pp. 299–300.

[2] DIELS, O., AND ALDER, K., *Ann.*, 460, 98 (1928).

The Experiment

Set up a fractional distillation assembly, for example, a side-arm distilling tube loosely packed with brass scouring sponge. The receiver should be cooled with an icebath to reduce the fire hazard. Place 15 ml of practical or technical grade dicyclopentadiene in a 200 ml round-bottom flask, attach, and heat moderately. Drive off the cyclopentadiene which forms on heating as fast as possible without flooding or foaming into the column, but do not exceed 65°C at the top of the column. Collect 7 ml of the distillate; no forerun need be collected. If the distillate is cloudy, dry it with a few grams of calcium chloride and decant.

Weigh 6.0 g of maleic anhydride and grind it to a fine powder with mortar and pestle; reweigh the powder after grinding if necessary. Avoid touching the powder or breathing the dust since it can irritate the skin and respiratory tract. Suspend in a 125 ml Erlenmeyer flask the maleic anhydride in 25 ml of dry benzene and cool, but do not freeze in an icebath (Note A). While still cooling, add, with swirling, a solution of 6.0 ml of cyclopentadiene and 5 ml of benzene (Note B). Swirl for several minutes—until a pasty precipitate appears. Warm the flask for 5 min on the steambath, then remove and add 30 ml of ligroin, bp 60–75°C (Note C). Swirl in the icebath until thoroughly chilled, then filter with suction. Press the crystals and rinse first the reaction flask and then the crystals with 5 ml of ice-cold ligroin.

Remove the crude adduct and place it in the same flask previously used (Note D). Dissolve in the minimum amount of boiling ethyl acetate on the steambath (Note E). Remove from the bath and add the minimum amount of ligroin needed to produce a few crystals. Heat on the steambath until the crystals dissolve. (If a few small crystals remain in spite of several minutes boiling, filter hot (Note F).) Allow the solution to cool slowly to room temperature, then cool the flask in the icebath and filter with suction. Press down the crystals and rinse with 5 ml of ice-cold ligroin. Spread the crystals on a tared watchglass and allow to dry in the air. When the odor of solvent is gone, record the weight and bottle quickly to avoid reaction with atmospheric moisture. Determine the melting point. (Diels and Alder reported 164–165°C; this work, 167–168°C.) A typical student yield is 70%.

Note A. Benzene straight from the drum is usually good enough. If not, it can be dried by distilling from it the water azeotrope. That is, distil until the distillate is not cloudy (about 5% of the total) and use the pot material.

Note B. The reaction is quite exothermic. If the materials are mixed with no solvent, the reaction goes with explosive violence. However, if the solutions mentioned here are handled according to the directions there is no hazard. If the two solutions are poured together without swirling and without cooling,

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the benzene will boil and foam over. A very little happens. A transitory yellow color is observed, which is probably due to the pi complex that forms initially. For a better illustration of this phenomenon, use benzene solutions of anthracene and tetracyanoethylene.[3]

Note C. Ligroin, petroleum ether, or mixed hexanes, all boiling 60–75°C, may be used.

Note D. As an alternative at this point, the corresponding diacid can be made and recrystallized as follows. Add 20 ml of water and heat to boiling. After a few minutes the solid will melt and mostly dissolve. If necessary, add more water to complete solution. Allow the solution to cool to room temperature, then cool in the icebath. Filter the crystals by suction, wash with 5 ml of ice-cold water and dry in an oven at 110°C on a tared watchglass. When it reaches constant weight, record the yield and determine the melting point. Diels and Alder reported 177–179°C; this work, 182–185°C with decomposition.)

Note E. All low boiling solvents should be heated on the steambath, not over an open flame. Ethyl acetate has a tendency to superheat; a boiling chip, to be removed later, is advisable.

Note F. This material is the acid formed when the anhydride reacts with water.

Comments

This experiment went well unless the student got water into the reaction. In this event, the alternative conversion to the diacid, Note D, is recommended. Both the anhydride and the diacid form very pretty crystals. A simplified mechanism involving the principle of maximum overlap of π bonds had been presented in lecture and was driven home in the prelaboratory discussion.[4] The preparation of cyclopentadiene by the dedimerization helped to illustrate the reversible nature of the reaction, which had been mentioned in the lecture. The students were also introduced to *endo-exo* isomerism, which they comprehended readily. They were interested in the nomenclature of the bicyclic compounds, but were not required to learn it.

Before starting work on this (or any other experiment), each student made a table in his laboratory notebook listing the amount of each material used, the number of moles used, physical constants such as melting point, boiling point, solubility (to the extent available in the usual handbooks). Likewise the physical constants of the products would be recorded if available. This allows the student to see whether the reagents are used in the stoichiometric ratio or not. He is expected to know why the particular ratio was chosen. The physical constants help the student to understand why the procedural details are chosen as they are.

Special projects starting with this compound might include the complete conversion to the *cis*-cyclopentane-1,2,3,4-tetracarboxylic acid by potassium permanganate oxidation. The double bond is quite reactive and might be hydrogenated by the use of palladium and tetralin, thus avoiding the use of pressure apparatus.[5] For the student with only a few minutes' time, a search of Beilstein for the physical constants involved would be a useful introduction to this important literature source. For a larger literature problem, a search for the method of proof of structure should be interesting.

[3] Schimelpfenig, C. W., J. Chem. Educ., **36**, A379 (1959).

[4] For a detailed discussion see Woodward, R. B., and Katz, T. J., *Tetrahedron*, **5**, 70; *Tetrahedron Letters*, **5**, 19 (1959).

[5] Wilen, S. H., and Kremer, C. B., J. Chem. Educ., **39**, 209 (1962).

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Student Preparation and Manipulation of a Gas—Methyl Ethyl Ether

In an effort to incorporate some newer techniques and reactions into an undergraduate laboratory program, we have studied some experiments which we feel are of general interest. It is the purpose of this report to note one such experiment. The experiment described here has been successfully employed early in a second semester organic chemistry laboratory and has been found to provide a useful gauge of the student's technique and ability.

Standard laboratory textbooks usually include under the subject "preparation of ethers" a synthesis involving either acid catalyzed dehydration of an alcohol to give a symmetrical ether such as diethyl ether or a nucleophilic displacement of an alkoxide on an alkyl halide (Williamson synthesis) to give a symmetrical or unsymmetrical ether such as diethyl ether, dibutyl ether or anisole. The preparation of methyl ethyl ether (boiling point 6.6°) (*1*) by a Williamson synthesis offers an excellent opportunity to demonstrate by analogy some of the principles of high vacuum line manipulation of gases without the actual employment of a vacuum or any elaborate or expensive equipment. The boiling point of methyl ethyl ether is sufficiently high to permit condensation and temporary storage at ice-brine temperatures; but it is sufficiently low that it is a gas at room temperature, thereby presenting problems which the student would not usually encounter—problems such that a student who fails to anticipate in advance the requirements of the experiment may fail to obtain the ether. A high purity of product will result only when strict adherence to appropriate bath temperatures and distillation rates is maintained during the series of four successive bulb-to-bulb distillations used for purification.

The instructor may verify weights or boiling points while the experiment is in progress or may elect to defer these observations until a later date, if this is done, student preparations may be stored in stoppered test

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tubes in a freezer for a long period of time. Quantitative analysis of student samples by GLC is recommended and under the conditions suggested here require only 3 or 4 min per sample for a complete analysis.

The reaction of sodium methylate and ethyl iodide rather than the alternative sodium ethylate and methyl iodide was chosen for several reasons: the boiling point difference between product and starting materials is greater in the former, favoring a purer product;

$$CH_3O^-Na^+ + C_2H_5I \xrightarrow{CH_3OH} CH_3OC_2H_5 + NaI \qquad (1)$$

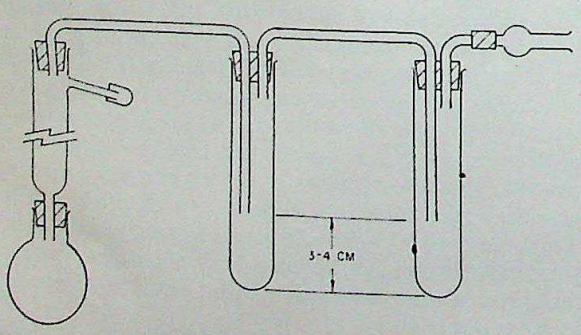
availability of dry sodium methylate as a commercial preparation does away with student-handling of substantial quantities of sodium in an experiment requiring the use of several water baths; and the sodium methylate-ethyl iodide combination is more economical, for the total cost of the experiment is estimated at about $0.65 per student.

Safety Precaution. The product of this experiment is volatile and highly flammable. For these reasons the experiment should be conducted in a well ventilated area in which no flames or electrical apparatus are in use.

Methyl ethyl ether has been frequently studied (*1*, *2*) and prepared (*3*) but has seen little chemical use. In laboratories where student preparations would result in a substantial amount of sample this ether might be considered for research use in the extraction of exceedingly volatile substances. In addition, the presence of two different simple alkyl groups on a basic oxygen atom suggests possible application to proton magnetic resonance studies of bonding in certain Lewis acid-base complexes.

The Experiment

The apparatus shown in the drawing is assembled and dried by flaming. The flask is 200 ml; and four 2.5 × 20-cm test tubes, each containing a boiling chip, are needed. *An additional safety precaution would be to insert a safety tube extending from the drying tube to the* floor. When the flask has cooled to room temperature, a 6.0-gm (0.11 mole) portion of sodium methylate is placed in it. The flask is then quickly covered with 40 ml of anhydrous methanol and replaced in the apparatus. (Sodium methylate (sodium methoxide) is extremely hygroscopic. It is advisable to preweigh the appropriate amount of this reagent into test tubes which are then corked and stored in a large screw cap bottle over Drierite. As a substitute 2.3 gm of sodium metal may be dissolved in 95 ml of anhydrous methanol, using external cooling. Due to the hazards of handling sodium metal and the flammability of the generated hydrogen, this procedure is not recommended.) The heat of solution is dissipated by swirling the reaction vessel in an ice bath during the addition. When the sodium methylate has dissolved and the solution is cool, the flask is removed and 15.6 gm (0.1 mole) of reagent-grade ethyl iodide is added rapidly in *one* portion, to prevent the introduction of moisture. *From this point onward, it is essential that all flames in the laboratory be extinguished. Because of possible sparks, no electrical apparatus should be near the area in which this preparation is being conducted.*



Position No. 1 Position No. 2 Position No. 3

The flask is 200 ml; four 2.5 × 20-cm test tubes, each containing a boiling chip, are needed.

The test tubes at positions No's. 2 and 3 are cooled by an ice-salt freezing mixture (−5 to −10°C) and the reaction is swirled intermittently for 15 min. The reaction flask is then heated by a gentle current of steam until gas evolution becomes smooth. The rate of heating is adjusted so that slow refluxing occurs about half-way up the column.[1] After about 45 min, gas evolution will cease. The reaction flask and column are removed and replaced by a clean *tared* test tube. The freezing bath at position No. 2 is then replaced by a warm water bath (45°C). The product will distill into the test tube at position No. 3, leaving behind a substantial amount of unreacted ethyl iodide and methanol.

The test tube at position No. 2 is removed and replaced by a clean test tube. In a smooth operation the test tube at position No. 3 is removed with its freezing bath and placed in position No. 1, while the clean tared test tube which was at position No. 1 is placed at position No. 3. An ice-salt freezing mixture is placed around the test tube at position No. 3; the freezing mixture is removed from the product at position No. 1, placed around the test tube at position No. 2, and the test tube at position No. 1 is immersed in warm water bath (40°C). The product will distill smoothly into the test tube at position No. 2, leaving behind a small amount of higher boiling material. When the distillation is complete the cold bath is removed from position No. 2 and replaced by a warm water bath (35°C). Practically all the material will now distill into the test tube at position No. 3.

The drying tube is removed from the apparatus and inserted in a one hole stopper. The freezing bath and test tube at position No. 3 are then removed, and the test tube is capped with the drying tube. This test tube containing the product may be wiped dry and weighed quickly without the drying tube to determine the yield. Two to four grams of methyl ethyl ether, a water-white liquid should be obtained.

The boiling point may be observed as follows: Into a two-hole stopper a thermometer is inserted so that it will be partly immersed in liquid when placed in the ether, but will not touch the sides of the tube. The test tube is then removed from the ice-salt bath, wiped dry and insulated at the bottom with several thicknesses

[1] We recommend a simple distilling column packed loosely with stainless steel sponge, as described in FIESER, L. F., "Experiments in Organic Chemistry," 4th ed., D. C. Heath and Co., Boston, 1957, p. 14.

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of dry paper towel. The tube is held so that it is not heated by the hands and is agitated continuously under a hood while the temperature is observed at 30 sec intervals until constant for at least 3 min. This value should be recorded as the boiling point of the liquid. If the sample is to be turned in to the instructor, the thermometer is removed and replaced by the drying tube; then the sample is placed in a dry-ice bath provided for this purpose.[2]

[2] To the instructor: Methyl ethyl ether may be quantitatively analyzed for purity by gas-liquid chromatography. All components are rapidly and cleanly separated by a column 18 × 1/4 in of tricyanoethoxypropane, TCEP, (4–6), on firebrick at 25°. Retention volumes are as follows: methyl ethyl ether, 24.8 ml; ethyl iodide, 135 ml; methanol, 315 ml. Careful regard for detail in this experiment will produce a product 92–95% pure (by GLC) at a yield of 50% of theoretical. A Perkin-Elmer model 154D Vapor Fractometer was employed for these analyses.

Questions

1. Why is it necessary to exclude moisture from the reaction? Illustrate your answer with an equation.
2. What is the side reaction product which would result from *elimination* rather than substitution? Write the equation. How would you detect this material?

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(5) Casanova, J., Jr., and Corey, E. J., *Chem. and Ind.*, **1941**, 1664.
(6) McNair, H. M., and DeVries, T., *Anal. Chem.*, **33**, 806 (1961).

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Magnesium Cell for Demonstration

Compactness, nonpolarizability, high ampere hour capacity, and simplicity of fabrication are some of the attractive features of the new cell system described here. This cell system consists of copper and magnesium plates or ribbon dipping into copper sulfate solution. A layer of insoluble material develops at the magnesium electrode as soon as the electrode is dipped in copper sulfate solution. This layer acts as a natural separator between anode and cathode, eliminates short circuiting, and so allows close packing of the electrodes in the cell. The internal resistance and volume of the cell is thus minimized. The copper sulfate solution used here acts as an electrolyte for the magnesium electrode and also as a depolarizor at the cathode. The cell system does not get polarized at any rate of drainage of current, and hence it is useful for continuous heavy discharge. Typical data are 6 hr of operation at 1.1 v at 100 ma current.[1]

Miniature Cells. Miniature cells can be made out of magnesium plate or magnesium ribbon. Magnesium ribbon can be loosely wound over or within copper articles of different shapes such as a copper washer (Figure 1*a*), or a copper or brass thimble (Figure 1*b*), or a plastic sheet (Figure 1*c*). Magnesium ribbon will act as one terminal and a copper wire connected to the copper electrode as the other. On dipping the assembly (1*a*, 1*b*) in $CuSO_4$ solution, or filling (1*c*) with copper sulfate solution in a glass or plastic box, the cell will start functioning.

[1] Mathur, P. B., and Paul, N. J., *Indian J. Appl. Chem.*, in press.

A water activated dry type cell can also be made using anhydrous copper sulfate in the assembly. The salt is not hydroscopic and so the dehydrated salt does not absorb a large enough amount of water to start the chemical reactions with the magnesium in the cell. The shelf life of the cell is therefore kept high.

Long Duration Cell. A cell can be made with a bulb fixed on the lid of the container. The cell may be filled with copper sulfate solution, the copper and magnesium terminals connected to the bulb, and the copper electrode dipped in the solution and the magnesium electrode left outside the cell (Figure 1*d*). At the time of emergency the magnesium electrode may be inserted into the cell and dipped into the solution. The cell will immediately light the bulb. Magnesium plate or an assembly where a long magnesium ribbon (25–30 in. long) is wound over a plastic sheet can be used in these long duration cells. Some copper sulfate powder can be added to the solution for maintaining the concentration.

[2] Mathur, P. B., and Paul, N. J., *J. Sci. Industr. Res.*, 19A, 12, 597 (1960).

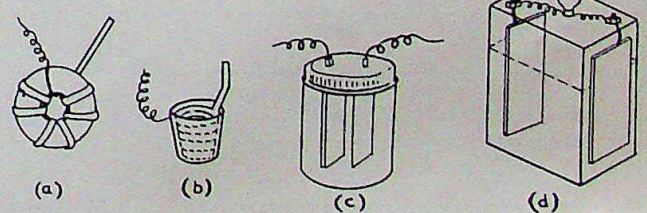


Figure 1. Miniature cells.

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Naming Chemical Elements in Chinese

In English we have the practice of naming chemical elements in Greek and Latin. Thus hydrogen is [ὑδρογένης (born of water), spelled out and slightly revised in Latin letters. It is interesting to glance at the systems of nomenclature used in a language which does not spell out its words in letters of an alphabet, and which, therefore, is ill-adapted to the assimilation of Greek and Latin. Such a language, of course, is Chinese. The supplementary volume of the encyclopedia *Tz'ŭ yüan* (Commercial Press, Shanghai, 1932) has a table on the basis of which one may distinguish four different ways of naming chemical elements in Chinese.

Ancient Names

Each of the 90 elements discussed in this table is described as discovered by a westerner during the period from the sixteenth to the first quarter of the twentieth century, except nine, which are said to be of prehistoric discovery. These nine are carbon, sulfur, iron, copper, tin, gold, mercury, silver and lead. The characters for metallic substances are formed from two radicals, with the exception of gold. The radical on the left side of the metallic elements is the character for gold. The radical on the left for carbon and sulfur means rock. The Chinese characters for these nine elements are an integral part of the language and literature and owe nothing to western terminology. See Figure 1.

Element		Character
carbon	*t'an*	碳
sulphur	*liu*	硫
iron	*t'ieh*	鐵
copper	*t'ung*	銅
tin	*hsi*	錫
gold	*chin*	金
mercury	*hung*	汞
silver	*yin*	銀
lead	*ch'ien or yuan*	鉛
radical for gold	*chin*	金
radical for rock	*shie*	石

Figure 1. Ancient names for elements.

Modern Names: Translations of European Words

Another small group of Chinese element names consists of characters describing qualities of elements in the same fashion as German. Thus, one way of saying (or, rather, of writing) hydrogen is to use two ideograms, *shui* and *su*, generating *shui-su*, which is an etymological equivalent for *Wasserstoff*. Another two-character rendition of hydrogen is *ch'ing-ch'i*, meaning etymologically a light, as opposed to a heavy, gas. In two other translations new characters have been introduced combining into single ideograms meanings contained in pairs of ideograms in the translations just cited. Thus, one of these single character translations for hydrogen is water inside of the gas radical, *Wasserstoff*, "born of water"; and the other is part of the symbol for light in weight inside of the gas radical. The whole character expresses in a single ideogram what *ch'ing-ch'i* said with two. (See Fig. 2.)

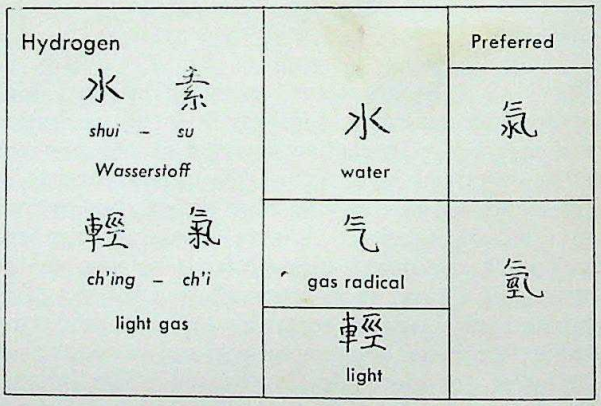


Figure 2. Chinese names for hydrogen.

A similar analysis may be given for the Chinese words for oxygen. One translation is *suan-su*, etymologically identical with *Sauerstoff*. Another is *yang-ch'i*, "the gas that nourishes." Two other translations are especially devised single ideograms, each enclosed by the gas radical, and inside of each a symbol pronounced *yang* and intended as a simplified form of the *yang* in *yang-ch'i* which means to nourish but is too complicated a pattern to fit inside of another. Of these two simplified *yang*'s, one is simpler than the other, and the translation of oxygen making use of this simplest *yang* is the preferred form. (See Fig. 3.)

Editor's Note: The author and editor gratefully acknowledge the assistance of Miss Helen Cheng Shan Li who executed the calligraphy for this paper. Miss Li was graduated from The College of Wooster in June 1962 with a BA in chemistry, and she is now a student in the Medical School of Stanford University.

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Nitrogen is *chih-su*, *Stickstoff*, also *tan-ch'i*, "tasteless gas," and *hsiao-ch'i* saltpeter gas. Again there are specially devised single characters with the gas radical on the outside and various ideograms pronounced *tan* (all standing for the *tan* that means tasteless) on the inside. (See Fig. 4.)

Oxygen		
酸 素	養 氣	氧 氣
suan – *su*	*yang* *ch'i*	*yang* *ch'i*
Sauerstoff	*nourish gas*	*preferred form*

Figure 3. Chinese characters for oxygen.

Nitrogen		
窒 素	淡 氣	硝 氣
chih – *su*	*tan* – *ch'i*	*hsiao* – *ch'i*
Stickstoff	tasteless gas	saltpeter gas

Figure 4. Chinese characters for nitrogen.

Aside from these three elements other translations presenting a description of quality and using single symbols expressly invented for the purpose, include phosphorus, platinum and bromine. *Ling*, phosphorus, combines the stone radical with a word meaning—when used without the stone radical—will o' the wisp. The ideogram for platinum consists of the metal radical and the character meaning "white." The only element in the table of 90 elements having a radical other than metal, gas, or stone is *ch'ou*, for bromine. Its radical is water and it is fused with a word meaning to stink. (See Fig. 5.)

Phosphorus		
磷	石	粦
ling	radical for rock	will o' the wisp
Platinum		
鉑	金	白
po	radical for metal	"white"
Bromine		
溴	氵	臭
ch'ou	radical for water	stink

Figure 5. Chinese characters for phosphorus, platinum, and bromine.

That several of these translations are precise etymological equivalents of German words would seem to indicate the influence of German chemical literature on China in the early twentieth century. The influence, however, was probably indirect: by way of Japanese translations of the German.

Modern Names: Transliterations of European Symbols and Words

If the reader will turn back he will remind himself that Chinese characters are analyzable into radical and phonetic, the former giving a clue to meaning, the latter to sound. The single character translations discussed in the preceding section are unusual in that their phonetics, although they suggest—as they should—the sounds of the characters they also—like radicals—help define the meaning. In the large class of single character translations to which we now turn, the phonetic is used exclusively in its proper function as phonetic, and tells nothing about qualities of elements. No doubt modern Chinese chemists were driven to this rather arbitrary method of naming elements for the simple reason that elements became too numerous and their identifying qualities too recondite to be expressed in the ideal ways described above. But in spite of a degree of arbitrariness, this newest of modern Chinese schemes of chemical nomenclature has all the ingenuity of Chinese genius. In the first place, it is inexhaustible and efficient, capable of turning out element names as if on an assembly line. In the second place, it enables the Chinese reader, to know at once to what class of elements a word refers, and to correlate the word with the European international chemical symbol or with the Latin or Greek name.

At least 60 elements are named according to this plan. Each name contains the classifying radical: metal, gas, or non-metal (stone), and the rest of the ideogram consists of a character which, as nearly as Chinese sounds permit, has either the same sound as that of the European chemical symbol, or the sound of some syllable (not necessarily the first) in the European name. For example: uranium, symbol U, is a character made up of the metal radical and a phonetic pronounced *yu*. Tungsten is the metal radical combined with *wu*, the first syllable of wolfram. Neon, symbol Ne, is the gas radical plus a phonetic pronounced *nai*. Arsenic is the stone radical with a phonetic pronounced *shên*, the second syllable of arsenic. (See Fig. 6.)

Uranium		
鈾	金	由
yu	metal radical	phonetic
Tungsten		
鎢	金	烏
wu	metal radical	phonetic
Neon		
氖	气	乃
nai	gas radical	phonetic
Arsenic		
砷	石	申
shen	stone radical	phonetic

Figure 6. Modern names for uranium, tungsten, neon and arsenic.

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This fourth and last of the Chinese ways of naming chemical elements need detain us only a moment. It has the ear-mark of an early experiment of translator's methodology, and it was soon abandoned. It consists of using ideograms as if they were syllables (like the Japanese *kana*) and actually spelling out the foreign word. Radium becomes *lei-t'ing*, where allowance must be made for the Chinese habit of using "l" for "r" in the transliteration of foreign words. Often the similarity of sound is difficult to hear. In some cases one wonders what happened, as in the case of *jih-chi-tê* for germanium. These symbols would mean "Japan and Germany" except that to each, including the "and," the metal radical has been affixed. (See Fig. 7.)

This system of representing foreign sounds has been used in China for many years, as readers of Chinese newspapers will recognize. Even in today's press the personal names of political leaders, scientists, etc., are still thus phonetized—just as in past centuries the names of people like Aristotle and Biblical prophets and apostles were phonetized. As far as personal names are concerned perhaps no other method of rendition in Chinese is possible. But Chinese chemists showed great wisdom in not attempting to develop that method for use in chemical terminology.

Radium 鐳 鋰 *lei* *ting*		
Germanium 鍺 鋨 鐿 *jih* *chi* *te*	日 及 德 Japan and Germany	

Figure 7. Modern names far radium and germanium.

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Translated by **Ralph E. Oesper**
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The Early History of Chemistry in Hungary

In 896 a Finno-Ugarian people from the Sarmatian Steppes north of the Black Sea migrated westward and pitched their tents in the basin of the Carpathian Mountains. They continued their warlike nomadic life for several decades and made devastating forays into Italy, Switzerland, and Bavaria. However, they encountered much stiffer resistance in Germany and after several defeats were glad to enter into a nine year's truce with Henry the Fowler, who bought them off with an annual tribute. Their duke Géza persuaded these intrepid semi-civilized horsemen that it would be better to take up a permanent residence. His son Stephen (997–1038) became a Christian and induced the tribesmen also to be baptized. Under his leadership, they made great political and cultural progress. He was crowned king in 1001, and this event may be taken as marking the beginning of the Hungarian state.

The Carpathian basin was rich in gold, silver, and copper. The deposits in Transylvania had been worked even by the Romans, and mining was carried on in Upper Hungary under Charlemagne whose empire had extended that far. The successors of Stephen I encouraged the production of these metals and conferred many privileges on the mining communities. During the Middle Ages, Hungary was the most important European producer of gold, silver, and copper.

Correspondingly, metallurgy and metallurgical chemistry were highly developed in this country. The metallurgy of Upper Hungary is repeatedly praised in the works of Paracelsus and Agricola. For example, copper cementation was invented there. Pieces of iron were placed in the mine waters to precipitate the copper that they contained. Of course no real explanation of the process could be offered; it was regarded as transmutation of one metal into another. The invention of the puddling furnace for reducing copper was also Hungarian, and from there the method was introduced in the 15th century into Germany and then into England.

The separation of gold from silver by nitric acid is first mentioned by Albertus Magnus (1193–1280). It appears that this method, the so-called "quartation," i.e., the separation by nitric acid of a 1:3 gold-silver alloy, was first used on a large scale during the fifteenth century in Upper Hungary.

The development of a metal industry required reliable analytical methods. The oldest of analytical procedures, cupellation of gold, was known in antiquity; and it was employed very early in Hungary. In 1342, the Hungarian monarch Charles I decreed that in every mining city there should be a royal house in which the samples of ore should be assayed before being smelted. The archives reveal that as early as 1450 nitric acid was an essential for the analyses, so we known that the wet method must have been used.

The first Hungarian University was founded about 1370 at Pécs by King Louis the Great. Natural sciences were practically non-existent at the time. The

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universities offered, at most, lecture discussions on the chemical elements within the framework and concepts of the scholastic Aristotelian philosophy.

Alchemy was practiced in Hungary, as it was in the other countries of Europe. The earliest proof of this is a papal decree issued in 1273 to the Dominican monastery at Buda, when the pontiff rebuked the monks for their alchemical activities and forbade them to continue such wordly endeavors. Among the Hungarian alchemists of later date were many noblemen, bishops, archbishops, and even a king and a queen.

The king who actively engaged in alchemy and whose laboratory journal has survived was Wladislaus II (1490–1516). There is no doubt that he was in need of gold no matter what the source. He was weak, his court was poverty-stricken, and even the royal table service was often in pawn. Louis II, son of Wladislaus, ascended the throne at the age of ten, and oligarchs who ruled in his name fought among themselves. Suleiman the Magnificent, the sultan of the Ottomans, seized the opportunity of a weakened Hungary and conquered and devastated large areas of the country in 1526. The remainder of the nation elected two rival kings who fought with one another. Tragic times followed. The western regions were Catholic under the Austrian Habsburg monarch, an independent Calvinistic duchy had been founded in Transylvania, and the Turkish domain was Muslim. Religious wars raged for 150 years. How could science develop under such circumstances? How could chemistry exist in such an atmosphere? Almost all that had flourished during the Middle Ages perished. The old institutions of higher learning disappeared.

During the religious wars of the 17th century, both parties founded schools primarily to promulgate their doctrines. Cardinal Pázmány recreated a university at Tirnau in 1635, and the Protestants founded several academies. Chemistry was not taught, but the Aristotelian and newly awakened atomistic theories contended in the philosophical teachings of the various schools.

Around the close of the 17th century, Hungary was liberated from the Turks by the Christian armies. The Habsburgs united Hungary under their crown. From then until 1918, Hungary and Austria existed as a dual monarchy, although the national sovereignty of Hungary was often little respected, if at all. Wars for independence resulted, but this protracted struggle was followed by an economic advance. Mining in particular was reorganized, and its progress was promoted by the founding of a mining school at Selmecbánya (now Banska Stiavnica, Czechoslovakia) in 1735.

The Mining Academy of Selmec

The school soon earned an international reputation as a seat of chemical training and research. Here for the first time in the history of the world, students received a practical laboratory training. In fact the founding decree directed that the students were to be instructed *practice et manipulando*. Furthermore, a list was given of the exercises to be performed in the chemical laboratory—primarily consisting of metal analyses. Most students came to the school from other European countries to learn the methods of metal production and assaying. Among them were a large number of Spaniards who practiced the profession in Latin America. Outstanding members of this group who had been trained at Selmec were Fausto d'Elhujar, who with his brother discovered tungsten (1783) and later became general director of the Spanish-South American mines, and Manuel del Rio, professor at the University of Mexico and discoverer of vanadium (1801).

When the French National Convention resolved to create a technical university (École polytechnique), the Selmec academy was cited as a model because of its progressive, practical curriculum (*1*). In 1763, the school at Selmec was promoted to the rank of academy, and various chairs were established, including a professorship in metal production and chemistry. The first occupant of the post (until 1769) was N. Jacquin, who later became a professor at Vienna. While at Selmec, he made a series of studies which completely substantiated Black's views about the causticity of quicklime, cutting the ground from under the then widely-held views of Meyer regarding the hypothetical *acidum pingue*, allegedly derived from the fire during the burning of limestone (*2*).

Antole Ruprecht, a graduate of the school, became its third professor. He experimented constantly. Conjecturing that the earths were compound materials, he attempted to reduce these earths. He constructed a furnace "which accomplished almost everything that had previously been achieved only by means of burning glass-heat and by fire blown with purest air. With the aid of this furnace all earths, including even the otherwise so infusible silica, could be quickly melted to a clear glass (*3*)." Ruprecht personally left no technical description of his furnace, but since he reported that he had melted even platinum in it, he must have reached almost 1600°C (*4*). With its aid, he attempted to reduce the various earths by heating them in mixture with powdered charcoal and linseed oil. He published a number of papers on his experiments and reported that he had succeeded in obtaining small metallic granules from the alkali earths (*5*). His findings attracted much notice and a vehement argument was carried out in the European journals. Klaproth in fact denied the theoretical possibility of "metallizing" the earths and believed that Ruprecht's metal granules were due to the impurities of the crucible (*6*). Davy's discoveries, which came not long after, proved without doubt that the earths were compounds and that consequently Ruprecht was theoretically on sound ground. Whether his metal granules were really calcium, barium, etc. or whether they actually consisted of the carbides of these metals cannot be decided.

Although somewhat farther removed from chemistry, mention should be made here of the international meeting held at Selmec in 1786. Perhaps it may be regarded as the forerunner of the international scientific congresses. It was convened for a rather interesting purpose. Ignaz von Born (1742–1791), Royal Commissioner of Coinage and Mining, invented a new process for the amalgamation of gold. In 1786, he invited experts from all parts of the world to view and study the installations which had been set up in Szkleno near Selmec. About 26 experts came from Germany, Spain, Mexico, Norway, and England. On this occasion at Selmec, Born organized the first international scientific society, and in 1790 its 154 members included

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such chemists as Lavoisier, Proust, Klaproth, Gmelin, Watt. Even Goethe was a member. Nothing much was heard about this organization later, and it is probable that it went out of existence because of the wars and political upheavals which began around this time.[1]

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Discovery of Tellurium

The discovery of tellurium was indirectly a consequence of Ruprecht's work. A puzzling mineral from Transylvania, nagyagite, appeared to contain considerable gold but did not yield a corresponding amount of the precious metal when processed. Ruprecht analyzed this ore in 1782. He came to the conclusion that it contained antimony along with the gold. Ferenc Müller von Reichenstein (1740–1825), one of Ruprecht's schoolmates and Director of the Transylvanian mines, replied to Ruprecht and stated that the ore could not possibly contain antimony; his investigation pointed to bismuth. Ruprecht responded that the constituent in question was certainly not bismuth. Müller admitted that he had been mistaken, asserting that they were dealing with a new metalloid. Thereupon, Ruprecht also reported that he too was now convinced that it could not be antimony. In 1783, Müller published a paper in which he reported that the ore actually did contain a new semi-metal which he called *metallum problematicum* (*7*). He enumerated the characteristic reactions of the element and closed his account by stating that he had sent a specimen to Tobern Bergman in Sweden with the request that his findings be tested. Bergman began this study and requested Müller to ship him more test samples. However, it is probable that Bergman never received them because he died two months after this letter of request. Müller then discontinued his study of this ore. Ten years later, Klaproth asked Müller for samples, analyzed the ore, and confirmed Müller's discovery. Müller did not suggest a name for the element and Klaproth then christened it tellurium.

Beginnings of Chemistry at the University

The university was transferred from Tirnau to Budapest in 1777. The first chemistry institute (department) was established by Maria Theresa in 1769, and Jakob Winterl (1732–1809) was appointed professor. Although he was guilty of many errors, Winterl acquired a reputation throughout Europe (*8*). It should be noted here that his lengthy tenure at the University had favorable consequences for chemistry in Hungary. He trained many men who became active in this field as teachers and investigators, and who in turn advanced this science in their native land.

The domination of Latin lasted longer in Hungary than in other countries; the official language was Latin until the beginning of the 19th century. The reports of the researches carried out at Selmec were published in German in a Viennese periodical. Chemistry textbooks were likewise written in these two languages. A nationalistic movement in literature set in at the end of the 18th century; it overflowed into politics at the beginning of the 19th century and soon made itself felt in science also. The first textbook dealing with chemistry written in Hungarian was published in 1800. The author, Ferenc Nyulas (1758–1806), had studied under Winterl. He encountered many difficulties because the necessary technical terms were non-existent in the Hungarian language and had to be created. "Nobody has made a Hungarian decomposition of water. It was much more difficult for me to construct the requisite expressions than to decompose water," he complained in the foreword. The first complete chemistry text written in Hungarian was that of Mihály Kovacs (1762–1851), also one of Winterl's students. Published in 1807, its composition presented many language difficulties to the author. Thereafter the Hungarian language came more and more into use in the chemical literature—by the 1860's it was employed exclusively in teaching and in the periodicals designed for reading within Hungary.

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(3) Westrumb, J., "Geschichte der neuentdeckten Metallisierung der einfachen Erdarten," Hanover, 1791, p. 10.
(4) Ruprecht, A., *Crells Chem. Ann.*, 1790 II, p. 200.
(5) *Ibid.*, 1790 II, pp. 3, 91, 195, 291.
(6) Klaproth, M. H., *Crells Chem. Ann.*, 1791 I, 119.
(7) Müller, F., "Physik. Arbeiten der einträchtigen Freunde," Vienna, 1783.

[1] Recent personal communication from Prof. Zoltan Gyulay, Miskolc, for which the author is grateful.

. . . the proton and neutron, which were once thought to be elementary particles, are now seen to be highly complex bodies. It is almost certain that physicists will subsequently investigate the constituent parts of the proton and neutron—the mesons of one sort or another. What will happen from that point on? One can only guess at future problems and future progress, but my personal conviction is that the search for ever-smaller and ever-more-fundamental particles will go on as long as man retains the curiosity he has always demonstrated.

R. F. Hofstadter
Nobel Price Lecture in Physics, Dec. 1961

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Report of the **New England Association of Chemistry Teachers**

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Tufts University
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Maxwell's Demon Demonstrator

Thermodynamics, for all of its fascination, does not lend itself to many physical demonstrations. Thinking that some teachers and their students might welcome an addition to the limited list, I should like to present the "Maxwell's Demon Demonstrator."

The basic demonstration is a simple variation of an old method for illustrating the concept of irreversibility. This first came to my attention in a "Larousse Scientifique"[1] which used examples similar to Figures 1, 2, and 3 to show the nature of an irreversible process. Figure 1 shows a sealed glass vessel having an elongated neck, held in an inverted position. Ten small spheres (five black and five white) have been sealed inside the vessel and rest in the neck in a definite order. In the illustration all of the black spheres are surmounted by the white ones. One might think of them as a layer of hot gas molecules lying above a layer of cold gas molecules. If the flask is tilted so that the spheres run out of the neck and mix in the body of the flask (Figure 2) an "irreversible" process has been performed. On reversing the tilting process, there spheres will run back into the neck of the flask but in an order which will probably not be the organized initial array. The arrangement will be randon, and might have the appearance shown in Figure 3.

This is the demonstration suggested by the Larousse reference. As it stands, it is excellent because it illustrates an irreversible process and also points out its statistical nature. It is not impossible that the initial array will be restored by reversing the tilting process. It simply is unlikely. Using five black and five white balls, the odds against reproducing the initial array are 252 to 1. If one thinks in terms of 5 cm^3 of hot gas and 5 cm^3 of cooler gas, rather than five black and five white spheres, consideration is extended to a greatly increased number of particles (molecules). On writing the probability expression for achieving an event wherein all the low temperature gas molecules precede all of the high temperature gas molecules into the neck of the flask, the truly formidable odds against this event are appreciated and insight into the nature of irreversibility may be gained.

Phase one of the demonstration is now completed. Repeated inversion of the irreversibility bottle will produce varying arrays, some distressingly close to the starting pattern. On a bad day, one might even achieve the original array. However, if the particular day is not a bad one, one now becomes conscious of a serious shortcoming in the demonstration. Because the bottle is sealed, it requires an inordinate amount of time to reconstruct the original array and ready the bottle for the next showing!

Here is a real situation that would benefit by the existence of Maxwell's Demon, and from the pedagogic point of view, an excellent opportunity to introduce the Demon concept. The concept of a minute, lightning-eyed intelligence who can effortlessly separate a random distribution of fast (i.e., hot) and slow (i.e., cold) molecules (or white and black spheres). Standing at an advantageous spot in the vessel he can pile up the molecules in carefully selected order. By destroying their random pattern as they dash wildly about in the flask he successfully violates the second law!

To emphasize the difficulty of the Demon's task one should now grasp the flask at the base of the neck, and,

[1] Urbain, G., and Boll, M., "La Science. Ses Progrés, Ses Applications." Librarie Larousse, Paris, 1934, p. 372–3.

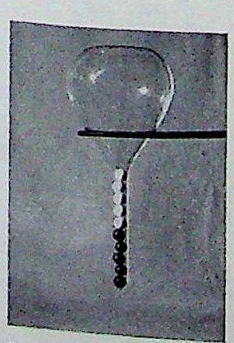


Figure 1. An organized array of particles.

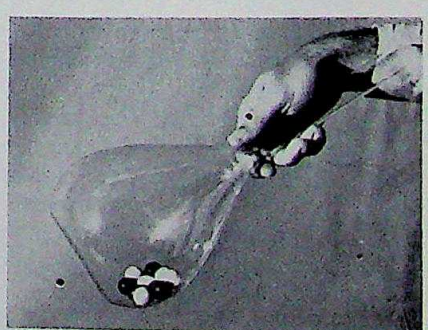


Figure 2. . . . subjected to an "irreversible" process.

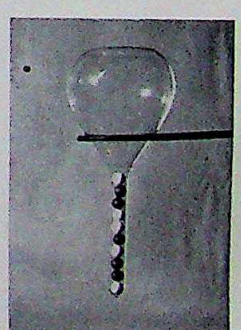


Figure 3. . . . cannot usually be restored by reversing the mixing process.

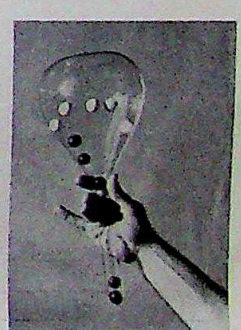


Figure 4. The "Demon" at work.

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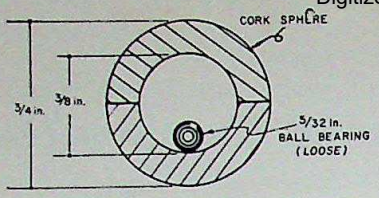


Figure 5. The Demon X-rayed.

holding it in a neck-up position so that the spheres remain in the flask body, rotate the flask briskly to impart a rapid swirling motion to the spheres. If the flask is now turned to the neck down position while continuing the rotation, the spheres will continue swirling wildly in the flask body, held there by centrifugal force.

At this point in the discussion one should remind the class, that no one, unfortunately, has ever succeeded in synthesizing or trapping Maxwell's Demon. The rotation can then be stopped.

When the motion of the flask ceases, the spheres whirling about in the flask body begin to lose momentum and follow an ever tightening spiral path into the neck. If this maneuver is performed with the proper flair, the behavior of the spheres as they enter the neck of the bottle may cause some observers to wonder about the true elusiveness of Maxwell's Demon. As the audience watches, the black balls spiral down into the neck of the flask followed closely by the white balls. As shown in Figure 4, the initial array is restored!

Class reaction reaches a maximum as the last white ball tumbles into place in its proper order. There usually follows a series of unsolicited explanations of this obvious bit of deception. "It's done with magnets!" "The balls are weighted!" Neither of the foregoing explanations is quite correct. The "demonability" resides in the fact that the black spheres are constructed so as to lose momentum very rapidly. They are hollow and contain within themselves some momentum absorbing means. A construction that has worked very successfully is shown in Figure 5.

The materials of construction for the Demon Demonstrator consists of ten $^3/_4$-in. diameter cork or plastic spheres, and a 2000 ml volumetric flask (Pyrex). Five spheres have the internal construction shown in Figure 5, and are painted a color which contrasts sharply with the five unaltered spheres. The neck of the flask should be about 8 in. long after sealing to accommodate the total number of spheres within its length.

Chem Ed

LETTERS

To the Editor:

The recent collection of articles on thermodynamics (the October, 1962, issue) is excellent. I want to congratulate you on having assembled it. The suggestions and approaches offered by the various authors should be helpful to all of us who attempt to convey to students the power of thermodynamic arguments.

I see one major lack in the collection. Nowhere is much real evidence given that thermodynamics is of aid to chemists. Isn't this too often the picture painted for the student? Thermodynamics is a beautifully knit, logical structure with an esoteric appeal all of its own. Just how and where chemists make use of it is never made more than a matter of passing reference. Its main output often seems nothing more than tables of data. My own feeling is that teachers of thermodynamics need to develop many more illustrative examples demonstrating the interpretation of chemical systems by means of thermodynamics. Current textbooks give little aid in such an enterprise.

Reaction of your readers and authors to this sally should be of considerable interest to me and to others.

Laurence E. Strong

Earlham College
Richmond, Indiana

To the Editor:

If examination papers are to be a teaching device, it is necessary to supply the answers; and this is usually done (if at all!) when the papers are returned.

At the time the corrected papers are returned, students are interested primarily in seeing their grades and only secondarily in discovering where they went wrong. After all, the next examination will cover new material. However, students are highly motivated to learn the correct answers at the time they leave the examination.

To harness this interest level, I hand out the mimeographed answers when the papers are turned in. This procedure immediately corrects mistakes and reinforces correct judgments, and thus acts somewhat in the manner of a teaching machine. A valuable side-effect is the saving in much lecture time formerly spent in going over examinations. Of course, important topics can still be reviewed. Also, final examinations which are usually never returned to the student can now serve an educational function. The minor disadvantage of preparing answers in advance is more than offset by the advantages of discovering beforehand the workability of the problems and how long it takes to solve them.

Rubin Battino

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Chem Ed

BOOK REVIEWS

Elements of Chemical Thermodynamics

L. K. Nash, Harvard University. Addison-Wesley Publishing Co., Inc., Reading, Massachusetts, 1962. ix + 118 pp. Figs. and tables. 15 × 23 cm. $1.75.

This book is intended to introduce chemical thermodynamics to the student of freshman chemistry. Included are discussions of the three thermodynamic laws and their "ideal" applications to thermochemistry, phase and chemical equilibria, and colligative properties. Calculus is used sparingly, and the elements of differentiation and integration are discussed in an Appendix. Consequently, the material is appropriate for beginning students who are concurrently enrolled in the first semester calculus course.

The subject development follows the usual path found in textbooks of physical chemistry and thermodynamics, but the material has been carefully simplified and organized so as to be palatable to the beginning student. It is clear that the author has used his sources well. To the initiate the exposition is lucid and smooth, although at times one wonders if the author's refreshing style doesn't move too fast for the beginner. Fortunately the arguments which involve or lead to chemical applications take precedence over the rather unexciting gas expansions which fill many more advanced texts. It is very important in introducing an abstract subject at this level to convince the student that the subject is worth learning, and this the author seems to have accomplished. Less fortunate, in this reviewer's experience and opinion, is the use of the Carnot cycle as a central part of the second law development. Nevertheless, the author has been more successful than most writers in answering the classic student question: What has the Carnot cycle got to do with chemistry?

Minimizing and simplifying the mathematics of thermodynamics is a difficult problem. In a neat sidestep of the dilemma of explaining exact and inexact differentials, the author uses the same symbol (q) to stand for both finite and infinitesimal quantities of heat. This works well until the temperature dependence of entropy is discussed and we are presented with the somewhat peculiar relation

$$\Delta S = \frac{q_{rev}}{T} = \int_0^{298} \frac{C_p dT}{T}$$

This and other such use of the first equation for nonisothermal finite changes may require some explanation.

The book is remarkably free from errors; the only one obvious to this reviewer is in Fig. 26, where it is log x and not its negative which is plotted. Included are a set of problems which do not require calculus and an ample table of thermodynamic data. The book should be of considerable help in introducing an useful improvement to the beginning course.

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Reviewed in This Issue

L. K. Nash, Elements of Chemical Thermodynamics
Martin Paul, Physical Chemistry
Eric Hutchinson, Physical Chemistry
George H. Duffey, Physical Chemistry
W. T. Elwell and *J. A. F. Gidley*, Atomic-Absorption Spectrophotometry
Børge Bak, Elementary Introduction to Molecular Spectra
Gordon M. Barrow, Introduction to Molecular Spectroscopy
Gregory R. Choppin, Experimental Nuclear Chemistry
Stanley Raimes, The Wave Mechanics of Electrons in Metals
E. G. E. Hawkins, Organic Peroxides: Their Formation and Reactions
Charles Tanford, Physical Chemistry of Macromolecules
Erich Heftmann, editor, Chromatography
Joseph S. Annino, Clinical Chemistry: Principles and Procedures
Robert Gould, editor, Borax to Boranes
Arthur I. Vogel, A Text-Book of Quantitative Inorganic Analysis Including Elementary Instrumental Analysis
Herbert C. Brown, Hydroboration

Physical Chemistry

Martin Paul, Harpur College, Endicott, New York. D. C. Heath and Co., Boston, 1962. x + 460 pp. Figs. and tables. 16.5 × 24 cm. $8.50.

To the array of recently published physical chemistry texts, Martin Paul has added a book of modest distinction. It lies between the extremes of rigorous dedication to the modern and the opposite adherence to the classical, but is closer to the latter. The presentation is fresh and intuitive.

Paul's "solution" to the difficult problem of what to leave out is to assume that atomic structure, X-ray crystallography, ionic equilibria and nuclear chemistry have now pervaded the introductory course in general chemistry and may appropriately be omitted.

His general plan is to demonstrate, whenever possible, the power of the thermodynamic approach. This is done in a pleasingly informal way. Kinetic molecular methods are used frequently, but these do not reach the "statistical mechanics" level. Thus his second chapter, the Conservation of Energy, moves in a natural way to a study of the gaseous state including the idea of using spectral information to evaluate energy states. The coverage of gas viscosity and thermal conductivity is relatively complete. Here as elsewhere in this book there are descriptions of important experimental methods. The problems appear to be very well chosen. Many of them are taken directly from the research literature. Answers are given for representative problems, and important examples are worked in the body of each chapter.

The fifth chapter covers both the liquid and the solid state using the common theme of intermolecular forces. This joint coverage is preferable to the complete omission of these topics.

Thermochemistry comes next. The development is rather extensive, including, for example, ionic enthalpies of formation and theoretical flame temperatures. The thermodynamic properties of gases and the second law of thermodynamics are developed concisely without extensive elaboration.

Vapor pressure is the theme of the next two chapters which deal with phase transitions and then with properties of solutions. Free energy is introduced at this point, long after entropy.

The chapter on Chemical Equilibrium begins with a conventional "law of mass action" development of the equilibrium constant. This is, of course, followed by a more rigorous thermodynamic treatment and ultimately reference is made to the use of molecular statistics. The coverage of Equilibrium for Nonideal Solutions is adequate, but not extensive. The phase rule is illustrated with numerous systems of practical importance, but with little use of thermodynamics.

The treatment of Rates and Mechanisms of Chemical Reaction is conventional except for the fairly complete consideration of two interesting examples of complex homogeneous reactions, acetone-bromine and hydrogen-bromine.

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The concluding chapter, Electrochemical Processes, covers both conduction and electromotive force.

The book is outstanding for its conciseness and freedom from error.

It is the feeling of the reviewer that the style, level of presentation and range of topics make this text especially worthy of consideration for a junior or even sophomore level course for students taking another chemistry course simultaneously and having calculus and general physics as prerequisites. Superior advanced undergraduates, no doubt, would find it less stimulating than texts that stress the more modern and advanced approach begun by Moore and continued by Barrow, Hutchinson and others. The omission of atomic and molecular structure may be its greatest weakness especially for curricula that do not include a course in atomic or modern physics. It is definitely not a text in "mathematical chemistry," but the attention paid to mathematics is adequate. The author is to be congratulated for a realistic and workmanlike job of discussing a rather traditional selection of material in an effective manner.

W. H. Hall
Bowling Green State University
Bowling Green, Ohio

Physical Chemistry

Eric Hutchinson, Stanford University, Stanford, California. W. B. Saunders Co., Philadelphia, 1962. x + 647 pp. Figs. and tables. 17.5 × 25.5 cm. $10.

Another very good entry has been added to the rather rapidly growing field of undergraduate physical chemistry textbooks. This book follows the trend, evident in several other recent books covering this area, of using a rigorous and sophisticated approach to the subject matter. Particularly noteworthy in this respect is the chapter on liquid solutions in which quantitative development of topics is used to a much greater extent than one is accustomed to find in undergraduate treatment of solutions. The author does not lose sight of the value of descriptive and interpretive approaches, and prudently intermingles these with the mathematical parts. Furthermore, the experimental side of physical chemistry is presented with detailed descriptions of experimental measurements of many important parameters.

Thermodynamics and its application to gases, liquids, solutions, heterogeneous systems, and electrochemical phenomena comprises the bulk of the material in the first half of the book. Chemical kinetics, atomic and molecular structure, solid state, macromolecules as well as a larger than usual portion of colloid and surface chemistry are covered in the latter part of the book. The last chapter is a brief but useful introduction to statistical mechanics. Notably absent in the book is any treatment of thermochemistry. Nuclear chemistry is also not treated.

An undergraduate physical chemistry textbook is, by necessity, an abridgement of the important developments of classical and modern physico-chemical research. This reviewer feels, however, that the omission of certain topics, such as thermochemistry, is unfortunate. In the chapter on the shape and size of molecules no mention is made of the important contributions of NMR to this area. The difference between path-dependent functions and point functions is another topic, well worth mentioning, which is excluded. The virtual absence of references in this book accents these omissions.

The problems at the end of each chapter are good and, in certain instances, quite challenging. An instructor's guide is furnished; it gives answers to problems and the method of solution for some. Several of the problem sets have many problems taken from the literature, an important factor in providing a sense of reality for the person attempting them. Very few example problems are worked out in the text. This will likely create difficulties for an average student, for the gap between some of the abstract sections of the text and the problems is wide indeed.

The illustrations and figures are done with precision and clarity throughout this work. They complement the material in the text very well.

Errors in the book are infrequent. Care should be exercised, as with any other book, in taking all equations at face value. For example, the kinetic theory formula on page 49 for $n_{E>E_0}$ is only an approximation as one can see by integration of the equation preceding it in the text. The approximation voiced by this equation is valid for $E_0 \gg nR\Theta$ (note also the omission of n_0 from the numerator of the equation and the omission of the subscript $_0$ from the E's). This equation may confuse some users of the book because its approximate nature is overlooked.

This is a book well worth an examination by a teacher of physical chemistry. Despite some omissions and a few uneven spots, it is a very good textbook.

Morley Russell
Michigan State University
East Lansing

Physical Chemistry

George H. Duffey, South Dakota State College, Brookings. McGraw-Hill Book Co., Inc., New York, 1962. x + 527 pp. Figs. and tables. 16 × 23.5 cm. $8.75.

It is inevitable that the next few years will see much discussion by teachers of undergraduate physical chemistry about how this course should be taught. The "classical" approach to this subject has usually begun with thermodynamics and other macroscopic properties of matter and has treated quantum mechanics, molecular structure, spectroscopy, and statistical mechanics at the end of the course as time permitted. More recently, however, physical chemists have been experimenting with a "non-classical" approach. In this treatment the course begins with a study of quantum mechanics, molecular structure, etc., and then develops and rationalizes macroscopic physical chemistry on the basis of the microscopic properties of matter. As one of the first American texts to use this "non-classical" approach this book is most welcome.

The book starts with a discussion of the structure of crystals and then follow chapters on atomic and subatomic particles, wave theory and its application to quantum mechanics, vibrational and rotational energy levels in molecules, electronic states in atoms, and basic valence theory. After this, the classical subjects of thermodynamics, chemical and physical equilibrium, activity concepts, and electrochemistry are treated. Finally the book closes with a discussion of kinetics, catalysis, and photochemistry.

The organization of the book is good with subjects following in a logical and very "presentable" order. The only exception that this reviewer would make is that statistical mechanics should be treated in a separate chapter instead of being divided between Chapters 7 and 9. This book has the advantages of the "non-classical approach" in that macroscopic properties of matter can be related to molecular and atomic properties without the background digressions necessary in the "classical" approach. Further, the undergraduate is quickly brought to the point where he can read modern physical chemical research results with some understanding. Strong points in the book that merit special mention are: the inclusion in Chapter 1 of a section on vector analysis, the treatment of the harmonic oscillator and the description of vibration-rotation spectra, the discussion of the properties of condensed phases, and the treatment of chemical kinetics.

The greatest weakness of the book is in its approach to quantum mechanics. The author develops quantum mechanics from wave theory, that is, the quantum mechanical wave function for a bound particle is equivalent to a standing wave set up by imposition of appropriate boundary conditions. It is the opinion of this reviewer that this approach to quantum mechanics is conceptually very difficult especially for students who have had no wave mechanics. A better approach might be the postulational approach in which the fundamental ideas of quantum mechanics are introduced as a series of postulates. Analogies can still be drawn from wave theory, but conceptually difficult discussions like the treatment of selection rules in rotation and vibration spectra in Chapter 4 could be avoided. In the absence of a lot of explanatory material in lecture, this reviewer feels that the average undergraduate physical chemistry student would have a difficult time getting through Chapter 3 and some parts of Chapters 4 and 5.

In summary, this reviewer feels that this book would make a good, but difficult, text in an undergraduate physical chemistry course for instructors who want to experiment with the "non-classical" approach. This is especially true for teachers who use a text for supplemental reading and not as an outline and description of the

(*Continued on page A54*)

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course itself. The book would also be valuable as a text for the second half of a "classical" course in physical chemistry. Chapters 1–6, a discussion of statistical mechanics and kinetic theory and Chapters 16–19 on kinetics would make a good second semester physical chemistry course.

MELVIN W. HANNA
University of Colorado
Boulder

Atomic-Absorption Spectrophotometry

W. T. Elwell and *J. A. F. Gidley*, both of I. C. I. Metals Division, Birmingham, England. MacMillan Co., New York, 1962. vii + 102 pp. Figs. and tables. 14.5 × 22 cm. $5.

Atomic-absorption spectroscopy was developed by Walsh in 1955 and rapidly became a sensitive method for the analysis of many metals in solution, particularly for certain samples not readily analyzed by methods of emission spectrometry. In this book the authors present a brief summary of the theory which is concerned with the intensity of spectral lines, the absorption coefficient of absorption lines broadened due to the Doppler effect and the need for a sharp line source. The equipment is described in a general manner, no details are given of vaporizers or burners required for handling the sample; however, the design and production of a hollow-cathode lamp is given. In the chapter headed General Consideration there is some discussion of the factors influencing the atomization of the liquid and the volatilization of the "clotlets" formed in the flame.

A list is given of 30 elements which can be determined, 10 of which receive special treatment in the remaining 50 pages of the text, with particular emphasis on zinc, lead, and magnesium for which detailed procedures are outlined.

The book is a reasonably good introduction to the subject but some recent journal articles have done almost as well. An extensive bibliography is given, useful for those who need to know experimental details that are lacking in this text.

THOMAS DE VRIES
Purdue University
Lafayette, Indiana

Elementary Introduction to Molecular Spectra

Børge Bak, University of Copenhagen, Denmark. 2nd ed. North-Holland Publishing Co., Amsterdam, 1962 (distributed by Interscience Publishers, Inc., New York). xi + 144 pp. Figs. and tables. 16 × 23 cm. $6.

The first edition of the little book by B. Bak, professor of molecular spectroscopy at the University of Copenhagen, was reviewed in THIS JOURNAL, 32, 222 (1955). This second, revised edition consists

(*Continued on page A56*)

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☐ **INORGANIC SYNTHESES, Volume VII**

By JACOB KLEINBERG, University of Kansas. Available in January, 1963.

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☐ **QUANTUM THEORY OF MOLECULES AND SOLIDS, Vol. 1 Electronic Structure of Molecules**

By JOHN C. SLATER, Massachusetts Institute of Technology. International Series in Pure and Applied Physics. Available in January, 1963.

In this timely work the author gives the most up-to-date treatment available of the rapidly changing field of the electronic structure of molecules, sometimes called quantum chemistry or molecular quantum mechanics. This is the first volume of a multi-volume series which will cover in an advanced treatment the entire field of modern solid state theory. The present volume covers the theory of the relatively simple molecules for which fairly complete theoretical discussions are available. The author has tried to develop the general methods of handling molecular theory, including the nature of the chemical bond and the symmetry of molecules, including a thorough discussion of group theory.

☐ **PHYSICAL AND CHEMICAL METHODS OF SEPARATION**

By EUGENE W. BERG, Louisiana State University, Baton Rouge. Available in January, 1963.

For the first time in a single volume, this text presents eighteen laboratory separation techniques. The author's aim is to enable the advanced student to recognize the inherent limitations of these separation methods and the type of system to which each method would be applicable. Emphasis is on the physical principles which govern the behavior of a given method. An effort is made to pin-point the important system variables, with a minimum of mathematical detail. Experimental detail is avoided through the use of schematic diagrams of the needed equipment with brief descriptions of the technique.

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essentially of the first edition in slightly larger format to which has been added a chapter of 17 pages on Magnetic Resonance Spectra. In the section corresponding to the first edition about 30 changes have been made. For the most part these have been the deletion, addition, or correction of a word or sentence. Since this reviewer agrees with the comments that were made in the review of the first edition he will make only a few general remarks.

Dr. Bak has attempted to write a monograph covering the whole field of molecular spectra in a form that is suitable for the non-spectroscopist. The treatment is extremely condensed and consequently it is very weak at exactly the places where the non-specialist needs the most help. The majority of the ideas, terms, symbols, and formulas encountered in molecular spectroscopy are mentioned but they are not amplified and for this reason the book is scarcely suitable for a person encountering this subject for the first time. Conceivably, the book would be useful to a person already familiar with molecular spectroscopy but desiring a compendium logically arranged.

Five-sixths of the new chapter is devoted to nuclear magnetic resonance and the remainder to electron magnetic resonance. The level is more elementary than the preceding portion of the book. Under NMR both the chemical shift and spin-spin interaction are discussed qualitatively and an attempt is made to explain the observed spectra in terms of paramagnetic currents, diamagnetic currents, and magnetically interacting spins. The three pages devoted to EMR do not allow the author to say very much. Several examples of the spectra of organic molecules are given in this chapter but the organic chemist cannot expect to learn much from such a cursory treatment of this important field.

Owners of the first edition will scarcely find it worth while to buy the second edition for the sake of the chapter on Magnetic Resonance Spectra. Others should realize the limitations of this monograph.

James Curry
Williams College
Williamstown, Massachusetts

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300 pages—illustrated. Published December 1962. $11.00

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52 Vanderbilt Avenue, New York 17, New York

Introduction to Molecular Spectroscopy

Gordon M. Barrow, Case Institute of Technology, Cleveland. McGraw-Hill Book Co., Inc., 1962. xiii + 318 pp. Figs. and tables. 17 × 24.5 cm. $10.75.

In some form or other molecular spectroscopy is used by a wide variety of scientists. The space chemist studying the combustion processes in rockets, the biochemist investigating photosynthesis and the theoretical chemist seeking to test his theories of bonding are but a few examples of the chemists who either use this type of spectroscopy as a tool or utilize the data obtained from it. Molecular spectroscopy is a rather specialized subject and the book reviewed here has been written with the aim of giving the non-specialist a deeper understanding of this field.

Dr. Barrow, an experienced teacher and contributor to the literature, has written on spectroscopy at a level between that found in physical chemistry textbooks and the specialized works represented by the classical books of G. Herzberg.

In this book theory is developed first and the results are then applied to a few examples. Schrödinger's equation is introduced in the first chapter and its use is illustrated by the simple particle-in-a-box problem. This leads to the application of the equation to the question of the energies in the π electrons of a conjugated system. Continual use is made of the equation in the later chapters.

Usually a subject is first treated by applying classical mechanics and the development is carried through the Lagrangian formulation. A good deal of emphasis is placed on the use of simple mechanical models that can be easily visualized. After that has been done fairly thoroughly, the quantum mechanical treatment is used, but here the methods of solution are often only sketched. Enough detail, however, is given so that the reader may understand what is going on. Finally, the refinements that are necessary to make the model more successful are pointed out and at times the corresponding equations are given. The development of the theory is logical and is very carefully done. Most readers will welcome the wealth of detail that is given

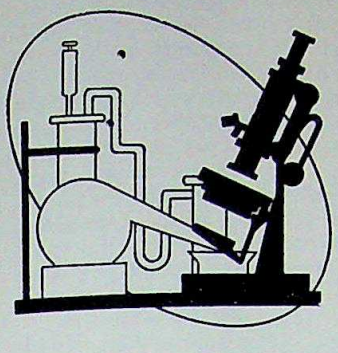
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By William F. Luder, Ph.D., Professor of Chemistry; Arthur A. Vernon, Ph.D., Professor of Chemistry; and Saverio Zuffanti, Professor of Chemistry, Department of Chemistry, Northeastern University, Boston, Massachusetts. 582 pages, 6" × 9¼", with 149 illustrations. $6.75. *Second Edition*

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By Garth L. Lee, Ph.D., Associate Professor of Chemistry; and Harris O. Van Orden, Ph.D., Professor of Chemistry, both of Utah State University. 637 pages 6" × 9¼", with 218 illustrations. $7.25.

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By Robert Fischer, Ph.D., Professor of Chemistry, Indiana University. 501 pages, 6⅛" × 9¼", illustrated. $6.75. (*Second Edition.*)

Lee and Van Orden—Lab Manual of General Chemistry

Designed for use in the 3-hour laboratory class, this manual can be adapted for the semester or quarter course. Tested in the authors' classes, each experiment promotes individual effort on the part of the student. Explicit instructions require a minimum of explanation by the instructor. Introductory experiments test laws and theories (equivalent weight, conductance, titration, etc.). Four experiments involve quantitative analysis. Organic experiments cover distillation, hydrocarbons, alcohols, esters, fats and oils, and preparation of aspirin.

By Garth L. Lee, Ph.D., and Harris O. Van Orden, Ph.D., 216 pages, 8½" × 11", illustrated. $3.75.

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These Texts Gladly Sent to Teachers on Approval

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in the mathematical steps. All of the specialized terms and symbols so peculiar to molecular spectroscopy are carefully explained.

The theory of rotation, rotation-vibration, and electronic spectra of diatomic and polyatomic molecules is covered. There is a chapter on adsorption and emission of radiation. This includes the derivation of the equation, unfamiliar to many chemists, which relates the integrated absorption coefficient to the transfer of molecules from one energy state to another.

The importance of the subject of the symmetry of molecules is emphasized and a separate chapter is devoted to it and elementary group theory. This material may be rather difficult for many chemists but it is essential for understanding the theory and is used in the following chapters.

In the final chapter theory is applied to the explanation of the electronic spectra of more complicated systems. The examples chosen are: formaldehyde, benzene, and several of the coordination compounds of the transition elements. Crystal field theory is used when appropriate.

A few miscellaneous comments are in order. Because there are adequate texts available on instrumentation and experimental techniques, these topics have been omitted. For the same reason there is no discussion of nuclear magnetic resonance or electronic spin resonance. Unfortunately only three lines are devoted to Raman spectra. A fair number of references, mostly to the standard specialized texts are given. Seventy-four exercises are distributed among the twelve chapters.

In summary, this in an excellent intermediate book on the theory of molecular spectroscopy. It is suitable as a reference book for seniors or to use in a graduate course or for self-study. Some nonphysical chemists may find parts of this book rather difficult but they will be amply rewarded if they work their way patiently through it.

James Curry
Williams College
Williamstown, Massachusetts

Experimental Nuclear Chemistry

Gregory R. Choppin, Florida State University, Tallahassee. Prentice-Hall Inc., Englewood Cliffs, New Jersey, 1961. xi + 226 pp. Figs. and tables. 16 × 23.5 cm. $6.95.

The impact of new areas of knowledge on the traditional fields of chemistry frequently goes through an interesting and similar pattern. Soon after the discovery of synthetic radioactivity, there was set in motion a flurry of experiments in which radioactivity was widely used in and stimulated some very intelligent research as well as being used in some trivial and unimaginative explorations. Over the last decade, this rather hectic and exciting period seems to be coming to a close, and is being replaced by a more orderly and thoughtful assimilation of the best that radiochemical techniques has to offer into the main stream of chemical science. Separate laboratory courses in the use of radioactivity have appeared during the transition period, although in many institutions radiochemical techniques have become an integral part of the traditional "technique" courses, at both the graduate and undergraduate level.

This well-written book will be useful in either of these situations. It was written directly for the uninformed non-specialist and student who wishes to enrich his experience by the addition of still another valuable experimental tool. This reviewer's opinion of the volume is that it is probably the best "technique" and laboratory book on this subject that has yet appeared. The experiments are designed to show something significant and illustrate the unique character and advantages of radiochemistry in a modest amount of time. Further, adequate explanation of laboratory safety, decontamination, and handling of radioactivity is given so that the less experienced teachers will have some feeling of adequacy in this area.

Perhaps some comments are in order that would have made the text just a little more useful. Liquid scintillation counting has become so very widely used

(*Continued on page A60*)

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for a wide variety of isotopes that it probably will shortly outnumber all of the other counting techniques and might have received more than just a casual mention. The advantages of this method are numerous, but the sources of difficulty are apparently largely unknown to many who attempt to use the technique. The treatment of neutron activation does not mention the possibility of producing (n, 2n), (n, p) and (n, α) reactions with fast neutrons which are always present in any neutron source. While the effective fast neutron flux may be much smaller than the thermal flux, the possibility of producing carrier free activities by the (n, p) and (n, α) reactions is occasionally useful.

The book is well bound and modestly priced and should find wide acceptance by teachers everywhere.

James W. Cobble
Purdue University
Lafayette, Indiana

The Wave Mechanics of Electrons in Metals

Stanley Raimes, University of London, England. North-Holland Publishing Co., Amsterdam, 1961 (distributed by Interscience Publishers, Inc., New York). xi + 367 pp. Figs. and tables. 16 × 23.5 cm. $13.

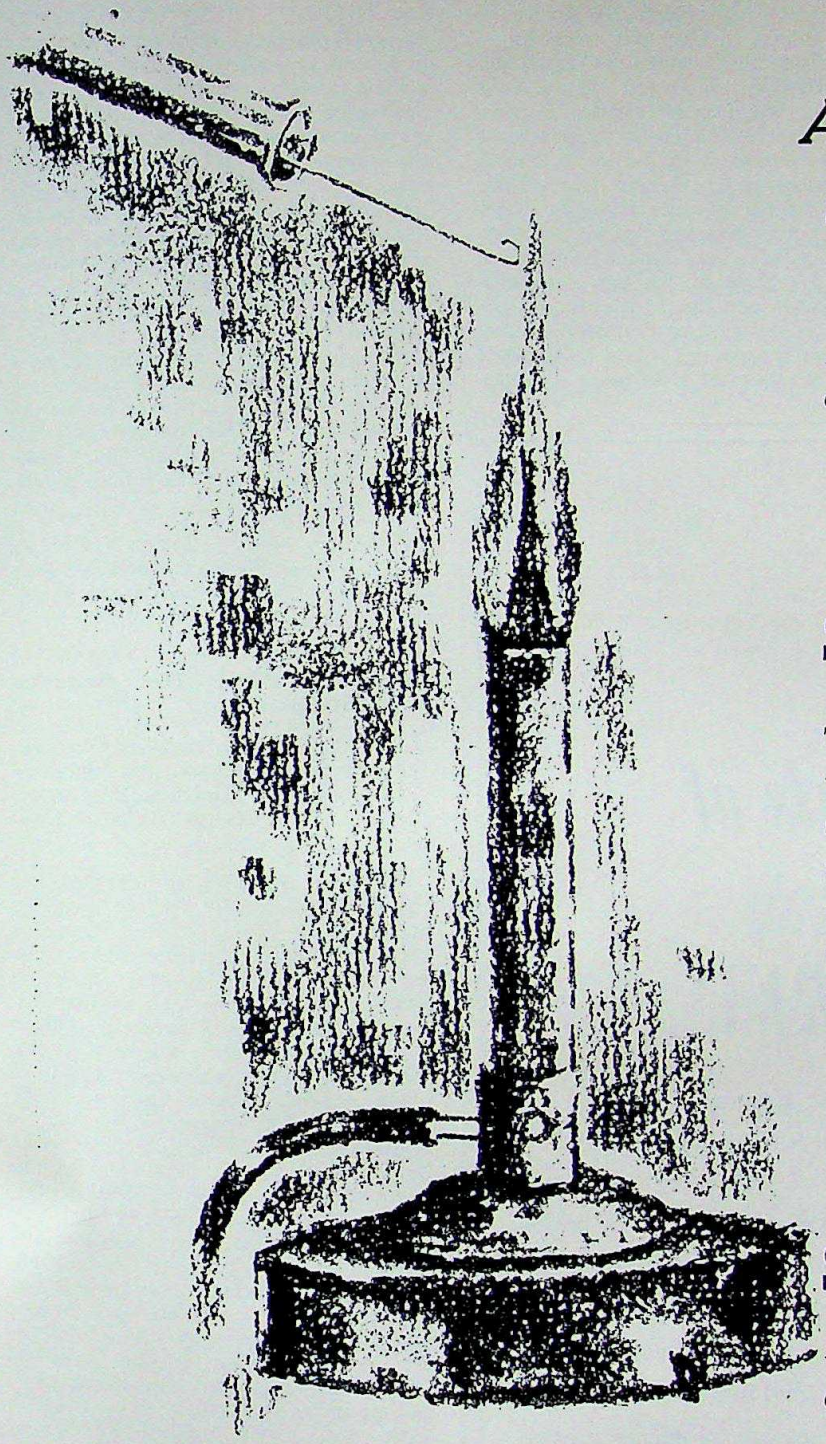
Dr. Raimes has written a book for the novice solid-state theorist, inquisitive experimentalist, and ambitious undergraduate in physics, chemistry, or metallurgy. He has restricted his subject matter almost exclusively to methods of calculating the cohesive energy of metals with particular emphasis upon the problem of treating the interaction of electrons in metals. In so doing, he has produced what one might call a "classical" description of the electron theory of metals, for none of the calculational techniques of the past five or six years is discussed. The reader is treated instead to detailed descriptions of the tight-binding approximation and the Wigner-Seitz cellular method. A dash of plasma theory is included in a separate chapter in order to make the one-electron approximation seem more plausible. The approach throughout is mathematical, and the accompanying text is both well written and lucid. The abundance of mathematical formalism should not frighten away the uninitiated, however, for all of the intermediate steps are presented. Moreover, the author has attempted to make plausible all of the approximations in the theory. The care with which the book has been written is reflected by the fact that it is almost totally free of errors, although this is its first printing.

Having selected a rather diverse audience, Dr. Raimes has elected to place them on an equal footing by first providing them with the basic concepts of wave mechanics. Consequently, the first third

(*Continued on page A62*)

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of his book is devoted to a formal development of wave mechanics which includes a discussion of the variational method, perturbation theory, the Hartree and Hartree-Fock approximations, electron spin and the Pauli principle. The hydrogen atom and molecule, and the helium atom are used repeatedly as examples throughout this portion of the book, making it easy for the reader to compare the results of varous approximate methods.

Most of the succeeding chapters cover theoretical methods for describing the behavior of electrons in metals: the free-electron approximation, Bloch functions and Brillouin zones, and a rudimentary treatment of plasma oscillations. The book is neither as sophisticated as those of Jones, Peierls, or Mott and Jones nor as nonmathematical as those of Cottrell and Hume-Rothery. However, it is not likely to prove satisfactory as the primary textbook for a first course in solid-state physics because of its failure to discuss applications of the theory. Thus, there is no mention of such topics as ferromagnetism or superconductivity. Moreover, although a final chapter is devoted to the implications of the time-dependent Schrödinger equation, there is no discussion of electrical conductivity or other transport phenomena. The book would appear to be most suitable as a supplementary text for a course in which a work such as that by Kittel or Slater is the main reference. It has the virtue of being self-contained owing to the inclusion of several appendices devoted to mathematical techniques, in addition to a set of problems for each chapter. Therefore, an ambitious student should be able to follow the arguments in the text without additional aid. In fact, if any criticism is to be leveled at the author, it is that he has done such a smooth job that he has not adequately prepared the serious student for the rough road ahead. His choice of sodium as a model, for example, tends to suppress the deficiencies in the theory. One suspects that he was motivated by a desire to bring some sense of satisfaction to those who do not intend to pursue the subject further. This approach is justifiable on the grounds that Dr. Raimes intends his book to be a primer on the electron theory of metals.

ALLEN N. GOLAND
U. S. Army Materials Research Agency
Watertown Massachusetts

18 | 17

fundamentals of College CHEMISTRY

Jesse H. Wood, Charles W. Keenan, William E. Bull, and Newell S. Bowman

Here is an introductory chemistry text which can be read and understood by the average college freshman. Designed for the nonchemistry major, this volume gives major emphasis to the general principles which govern the science of chemistry rather than to the more advanced and specialized areas of inorganic and industrial chemistry. Examples and step-by-step methods of solving problems are included. Exercises at chapter ends. 215 illustrations. *Laboratory Manual for General College Chemistry*, 2nd ed. (Harper & Row; 228 pp.; $3.25), by Smith and Wood, is suitable for use with this text.

Coming February 15

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Organic Peroxides: Their Formation and Reactions

E. G. E. Hawkins, Distillers Co., Ltd., Surrey, Great Britain. D. Van Nostrand Co., Inc., Princeton, New Jersey, 1961. xiv + 434 pp. 16 × 25.5 cm. $12.50.

This book provides a very complete and classified bibliography for the synthesis and reactions of the various classes of alkyl peroxides and hydroperoxides. The description of most journal articles is sufficient to determine their applicability to a particular area of research. This is therefore an invaluable reference volume for any investigator in this general field.

The subject of peroxides is so broad that the author necessarily has had to exclude or minimize certain topics while emphasizing others. The kinetics of peroxide reactions and a detailed discussion of their use in polymerization is completely omitted. Acyl peroxides are covered in very brief form. In contrast, roughly three-fourths of the book is devoted to alkyl peroxides and hydroperoxides of various types. A useful chapter on autoxidation is also included. The particular topics emphasized have not received very much attention in other texts and review articles. Therefore this book complements and does not duplicate the existing literature.

The hydroperoxides and peroxides are each classified into sub-groups by structural differences (e.g., acyclic, cyclic, heterocyclic, etc.). Within each subclass, synthesis is discussed first, followed by a description of the reactions.

The literary style and presentation of the topics leaves much to be desired. Principal patterns of mechanism are not delineated but instead are obscured by an infinite number of side reactions. The reader is left with the task of sifting out the most significant information.

The author has made this exhaustive compilation with very little critical commentary. For example, in the chapter

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on peroxide analysis, multiple procedures are given without any suggestions as to relative merit which would guide a research man entering into a new field.

The book is therefore an invaluable reference source for specialists in the field but is extremely difficult to read. It is therefore useless as a text for either classroom use or for self study.

RALPH DANNLEY
Western Reserve University
Cleveland, Ohio

Physical Chemistry of Macromolecules

Charles Tanford, Duke University, Durham, North Carolina. John Wiley & Sons, Inc., New York, 1961. xiv + 710 pp. Figs. and tables. 16 × 23.5 cm. $18.

Tanford's "Physical Chemistry of Macromolecules" is, in this reviewer's opinion, an excellent and worth-while book. Its merit lies not only in the contents which it covers, but more so in the manner in which the material is treated. This is done in an original, stimulating, and logical fashion, leading up from simple principles right into the full meat of the matter with many ramifications for general understanding and research. Especially noteworthy chapters are those on light scattering and on polyelectrolytes.

In view of the high quality of what is presented, one misses a fuller treatment of many neglected areas, although it is recognized that in order to keep the volume within a certain size sacrifices were necessary. Still these sacrifices are not too well balanced. For a book leaning so heavily on transport processes the hydrodynamic section is all too brief and incomplete. The chapter on thermodynamics following a rather elaborate one on chain statistics, does not make any mention at all of the thermodynamics of reversible chain contraction and extension but focuses entirely on the mixing problem. Thus, it is impossible for the reader to obtain appreciation of the effect of shear dependence on all transport processes, viscosity in particular.

Again, these criticisms do not refer to what the book contains but to what is omitted. Maybe the book should have been more clearly labeled as the physical chemistry of macromolecules in solutions, the topic it mostly deals with. The second chapter on molecular structure, which is in itself excellent and deals largely with structure in the solid state, is therefore outside the frame of the remainder of the book.

In conclusion, from the point of view of didactic approach and instrument of teaching, and advance information, the book can be highly recommended for the areas which it covers.

FREDERICK R. EIRICH
Polytechnic Institute of Brooklyn
Brooklyn, New York

Chromatography

Edited by *Erich Heftmann,* National Institute of Arthritis and Metabolic Diseases, National Institute of Health, Bethesda, Maryland. Reinhold Publishing Corp., New York, 1961. xxv + 753 pp. Figs. and tables. 16 × 23.5 cm. $17.50.

The field of chromatography and electrochromatography has expanded very rapidly in the past fifteen years, and "Chromatography," edited by Erich Heftmann, provides a complete, up-to-date reference volume in this field. The book is written by a number of scientists from various countries, each man contributing information in his specialized area. In general it is both authoritative and complete and should prove to be a valuable reference.

Divided into two parts, Fundamentals of Chromatography and Applications of Chromatography, the book provides a theoretical and descriptive account as well as the practical details and necessary references required for a particular separation problem.

In Part I, Fundamentals of Chromatography, the various types of chromatography are brought together and discussed under the headings of Adsorption, Partition, Ion Exchange, Molecular Sieve, Gas and Electrochromatography. The theoretical aspects of these various types

(*Continued on page A64*)

18 17

elementary Quantitative ANALYSIS, 2nd ed.

W. J. Blaedel and V. W. Meloche

This widely adopted text has now been updated and clarified. Outstanding for both majors and nonmajors and eminently teachable, the book now has new experiments, new questions, and problems, and a treatment of the importance of reaction rate in analytical chemistry. Closely adhering to Brönsted's acid-base theory, the text requires unusually high standards of accuracy. "Certainly deserves consideration by every teacher of quantitative analysis.... Simple and clear.... An abundance of well-chosen figures and tables.... Questions and problems... are thought-provoking." *Journal of Chemical Education*

Coming in April

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BOOK REVIEWS

of chromatography are discussed in separate chapters, each followed by a chapter describing the experimental techniques. Teachers and advanced students should find this section of the book to be of tremendous help in obtaining and understanding the fundamental principles of chromatography.

Part II, Applications of Chromatography, is divided into a number of chapters covering the possible methods of chromatographic separation for such compounds as amino acids, proteins, carbohydrates, lipids, alkaloids, etc. Rather than covering the entire field of chromatographic procedures for each type of compound, the reader is referred to already published monographs and reviews, and the material presented is primarily those techniques and applications which have been developed in the last few years. This section should be of extreme value as a reference book to chemists, biochemists and biologists who are active in the field of research.

BURK A. DEHORITY
Ohio Agricultural Experiment Station
Wooster

Clinical Chemistry: Principles and Procedures

Joseph S. Annino, Massachusetts Memorial Hospital, Boston. 2nd ed. Little, Brown and Co., Boston, 1960. xviii + 348 pp. 16 × 24 cm. $8.

This second edition is "designed to be of assistance to clinical pathologists, medical technologists, students of clinical chemistry, and to others who are concerned with setting up and controlling methods in the hospital chemistry laboratory."

An introductory Part I deals with such basic techniques and fundamental information as the use of the analytical balance and other concepts covered in elementary quantitative analysis. In addition there are pages dealing with laboratory planning, utilities, and first-aid suggestions. In an effort to keep the explanations quite simple, some rigor has been sacrificed. Thus, *p*H is defined in terms of the hydrogen ion concentration rather than its activity, and no mention is made of the rather important fact that the pK_w of pure water (and hence its *p*H) varies with temperature. In the colorimetry section, the term "optical density" is used instead of "absorbance" and the abbreviation "D" is used instead of "A_s."

There is a valuable chapter on sampling and tables of normal values for blood and cerebrospinal fluid are given. Control procedures, which are assuming increasing importance in most clinical laboratories, are treated too briefly to be of very much value. However, the use of standard curves is discouraged and it is strongly recommended that a dependable standard should always be run along with every unknown whenever possible.

(Continued on page A66)

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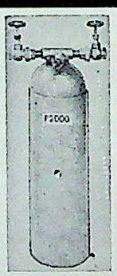


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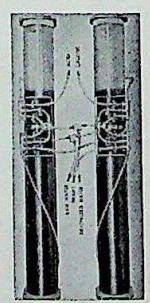
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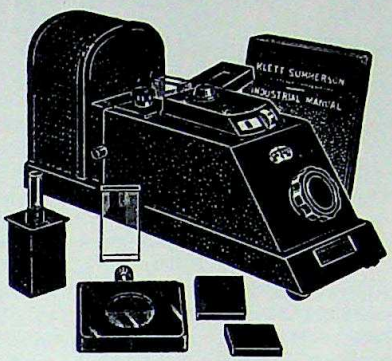
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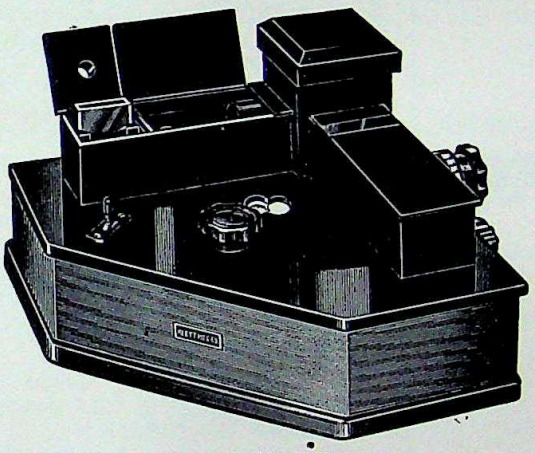
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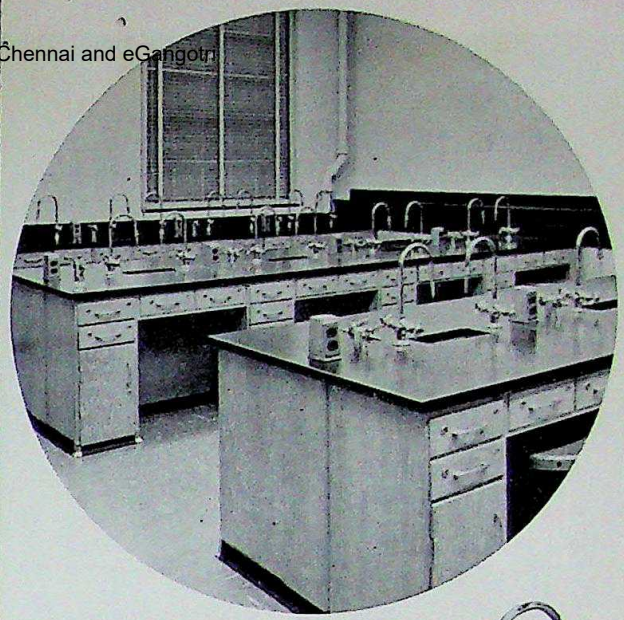
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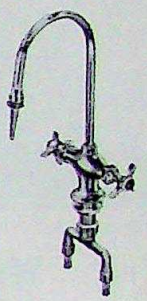
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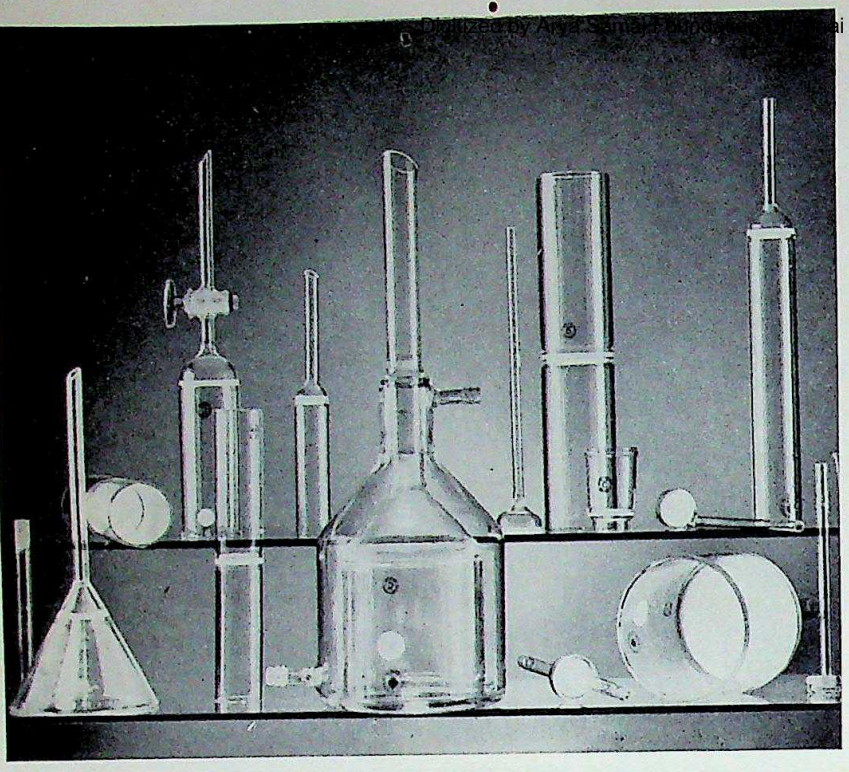
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In the Part II methods section, most of the common clinical procedures are covered although no mention is made of the very popular micro CO_2-content method using the Natelson gasometer nor of the newer coulometric chloride procedures. Indeed, in the chloride procedure described, one is surprised to note on page 96 that the orange color at the end-point is caused by molecular $Fe(CNS)_3$ rather than the $FeSCN^{++}$ or similar ion.

However, in spite of such statements as the above and references to an "orange chromate ion" on page 91 and the calculation of a NaCl concentration in urine from a chloride analysis, the author is to be commended for seeking explanations for many of the pitfalls in these procedures. The brief discussion of the physiological significance of the results should interest many workers in this field. Unfortunately, eight pages near the end of the reviewer's copy were difficult to read because of bad "print-through" from either the preceding or the following pages.

Many newer determinations have been incorporated into this edition, which like the original edition, was written especially for those just starting in the field. More experienced workers will doubtless prefer one of the more comprehensive treatises, but they, too, might find some valuable and practical hints in the discussions of the methods.

HAROLD E. WILCOX
Birmingham-Southern College
Birmingham, Alabama

Borax to Boranes

Edited by *Robert Gould*. Advances in Chemistry Series, No. 32. American Chemical Society, Washington, D. C., 1961. viii + 244 pp. Figs. and tables. 15.5 × 23.5 cm. $5.

"Borax to Boranes" is a collection of 27 papers which were presented at the 133rd ACS meeting in San Francisco, 1958. Although several papers are literature reviews, containing extensive bibliographies, the papers in general are research reports. Borane chemistry is not systematically covered, especially with respect to the higher boranes.

General topics treated can be placed in the following categories: 1, Papers covering historical aspects of boron chemistry; 2, Organoboron chemistry, including borocyclo-alkanes, boroxines, and borazines; 3, Reactions and properties of the boron hydrides, including the formation of saltlike compounds; 4, The preparation and chemistry of elemental boron and binary borides; 5, Mechanisms of acid-base and isotope exchange reactions; 6, Inorganic polymers; 7, Structures of crystalline boron, $NH_3B_3H_7$, and $(NH_3)_2BH_2Cl$; 8, Application of infrared and mass spectrometry to the study of boron hydrides and alkyl boranes.

It is unfortunate that this series of

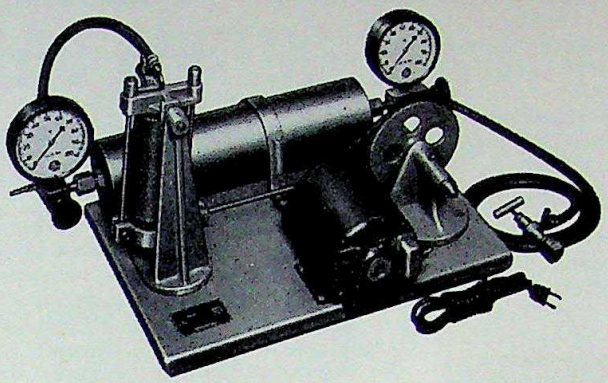
(*Continued on page A68*)

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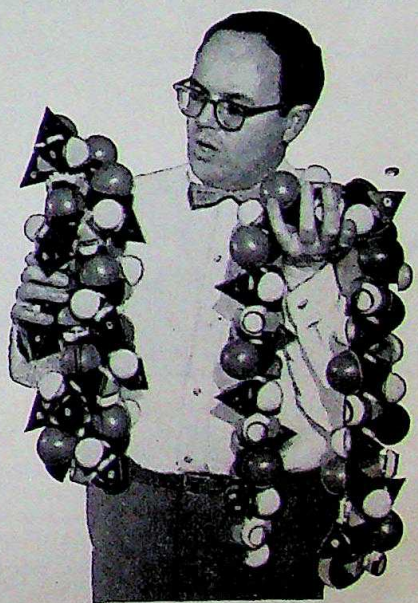
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papers was not published at a much earlier date, since several of the articles are no longer timely. Furthermore, the review articles covering organoboron chemistry, borazine chemistry, and inorganic polymers have been superseded by more recent monographs and review articles such as: W. Gerrard, "The Organic Chemistry of Boron," Academic Press, New York, 1961; H. C. Brown, "Hydroboration," W. A. Benjamin, New York, 1962; J. C. Sheldon and B. C. Smith, "The Borazoles," *Quart. Rev.* (London), XIV, No. 2, 200 (1960); F. G. A. Stone and W. A. G. Graham, "Inorganic Polymers," Academic Press, New York, 1962. Nevertheless, this book still serves a useful purpose to the specialist. The following papers are considered, by this reviewer, to have special merit in that they have no counterpart in the readily available literature, or in that they summarize information more thoroughly than other existing articles.

"Preparation and Chemistry of Elementary Boron" by A. E. Newkirk is a review containing 125 references. The most recent reference is dated 1959.

"Structure and Polymorphism in Elemental Boron" by J. L. Hoard is a more extensive treatment of this topic than that given by the same author in "Boron Synthesis, Structure, and Properties," Plenum Press, New York, 1960.

"Kinetics and Mechanism for Acid-Base Reactions Involving Boranes" by S. H. Bauer is a review containing 94 references. The most recent reference is dated 1959.

"Mass Spectrometry in Boron Chemistry" by I. Shapiro, C. O. Wilson, J. F. Ditter, and W. J. Lehmann discusses the application of mass spectrometry as an analytical and structural tool as applied to boron hydrides and alkyl boranes.

"Infrared Spectrometry in Boron Chemistry" by J. Lehmann, C. O. Wilson, J. F. Ditter, and I. Shapiro discusses the application of infrared spectrometry to structural problems in boron chemistry and summarizes vibrational effects of isotope and alkyl substitution on diborane.

"Metal Boron Hydrides" by M. V. Hough and L. J. Edwards discusses complex metal-boron-hydrogen compounds other than those containing the BH_4 unit. The authors evaluate the classic studies of Stock on reactions of alkali metals with the boron hydrides and then extend the discussion to relatively recent studies.

"The Unusual Salts Derived from the Boron Hydrides" by G. W. Campbell, Jr. is essentially an extension of the preceding article, covering salts in the boron-nitrogen and boron-oxygen systems as well as boron hydrides salts. This article contains 41 references and is an excellent summary of information available through 1958.

SHELDON G. SHORE
Ohio State University
Columbus

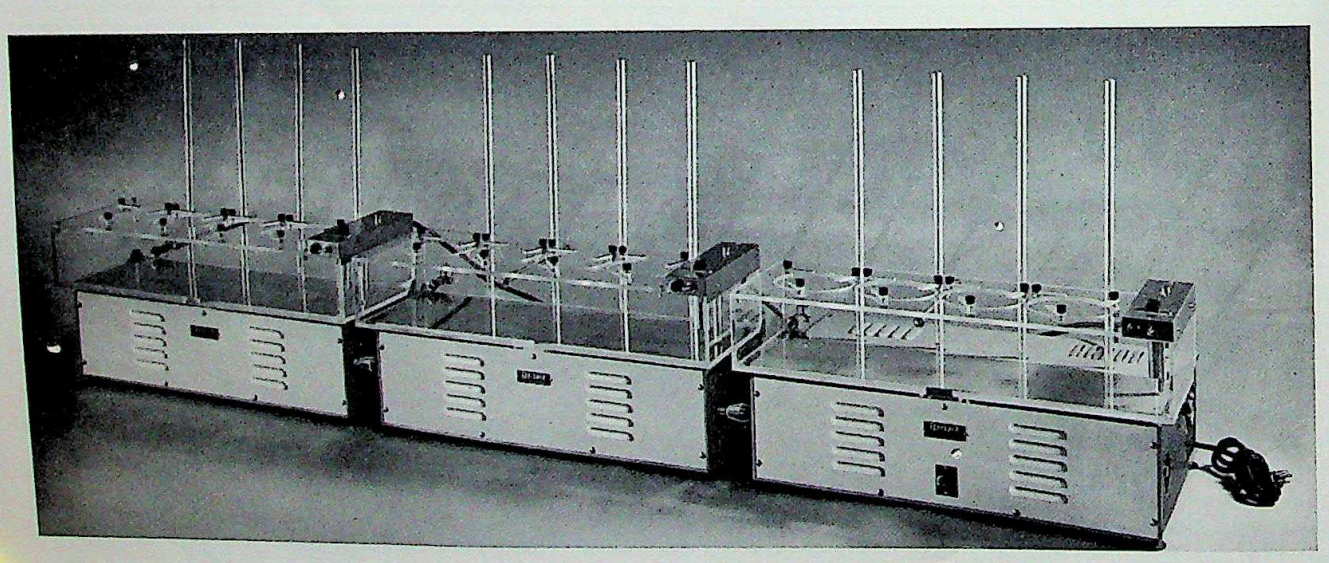
A Text-Book of Quantitative Inorganic Analysis Including Elementary Instrumental Analysis

Arthur I. Vogel, Woolwich Polytechnic, England. 3rd ed. John Wiley and Sons, Inc., New York, 1961. xxx + 1216 pp. Figs. and tables. 15.5 × 23.5 cm. $15.

The stated aim of the author in the preparation of this book has been to provide a textbook which would be of value both to the student during the period of his training and also his subsequent career, and also to the practical analytical chemist or the laboratory worker who may have occasion to use the methods of quantitative inorganic analysis. In the opinion of the reviewer these aims have been admirably fulfilled. There might be some question as to the desirability of this volume to be used solely as a student textbook, largely because of its size (1216 pages) and the very great amount of material contained in it. On the other hand, as a combined textbook and reference book it appears to have no equal. Indeed, this book would perhaps be consulted more frequently than any other single volume in the library of the analytical chemist.

In preparing the third edition of this well-known work the author has recognized the drastic changes which have occurred in the practice of analytical chemistry in recent years, and has, therefore, greatly expanded the topics which have been presented to include a comparatively

(*Continued on page A70*)



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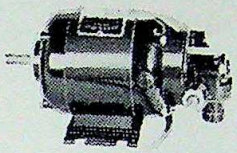
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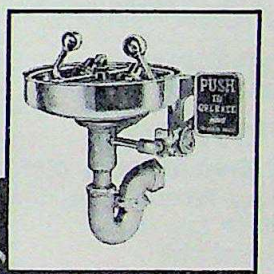
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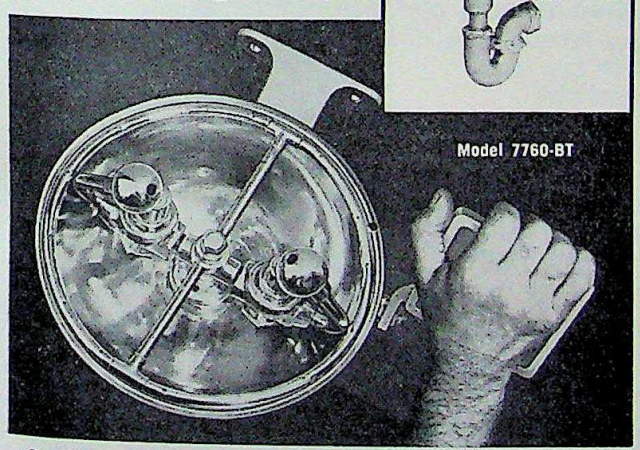
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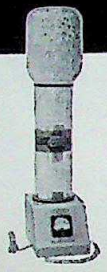
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BOOK REVIEWS

large amount of material on elementary instrumental analysis. New chapters which did not appear in the previous edition are: Complexometric Titrations (largely EDTA), Colorimetric Titrations, Ion Exchange and Chromatographic Methods in Analysis, Fluorimetric Analysis, Nephelometric and Turbidimetric Analysis, Emission Spectrographic Analysis, Flame Photometric Analysis, Solvent Extraction Methods of Analysis, and High Frequency Titrations.

Topics omitted because of lack of space are: X-ray methods, mass spectrometry, Raman spectrography, gas chromatography, radiochemical methods, nuclear magnetic resonance spectroscopy, polarimetry, refractometry, non-aqueous acid-base titrations, and significance of reaction kinetics in analytical chemistry. The omission of some of these is understandable, but, on the other hand, some consideration of non-aqueous acid-base titrations, gas chromatography, and radiochemical methods would have been desirable. This could have been done, perhaps, by eliminating a part of the fairly extensive material on classical methods.

The author is of the opinion that a proper appreciation of modern analytical chemistry requires an adequate preparation on the part of the student in the methods of classical analysis. For this reason a very considerable part of the book is devoted to gravimetric and volumetric analysis. Perhaps the classical methods have been too much emphasized, but in view of the stated purpose of making this book a reference book, it may well be that the inclusion of this material is desirable. In any event, the methods described are proved methods and are generally the most useful available.

The book contains a very large number of detailed procedures, utilizing essentially all common techniques, for most of the elements and most of the common anions. These methods are practical methods which have been established by use, and are not included simply to illustrate the various techniques which are described. This establishes the book as a reference book for the worker who requires practical methods for analysis. For this reason alone this book should be extremely useful.

The many new sections on instrumental analysis are brief and introductory in character, but they serve admirably to acquaint the analyst or the student with the analytical usefulness of the technique. In each of these chapters there is an excellent, though usually brief, discussion of the method. This is followed by a description of the instruments used, a number of practical determinations, and a selected bibliography.

The theoretical basis of quantitative inorganic analysis is clearly presented in an excellent chapter of 139 pages. The fairly lengthy discussion of the fundamental experimental techniques of inorganic analysis is also very well done and up-to-date. This is particularly noted in

(*Continued on page A72*)

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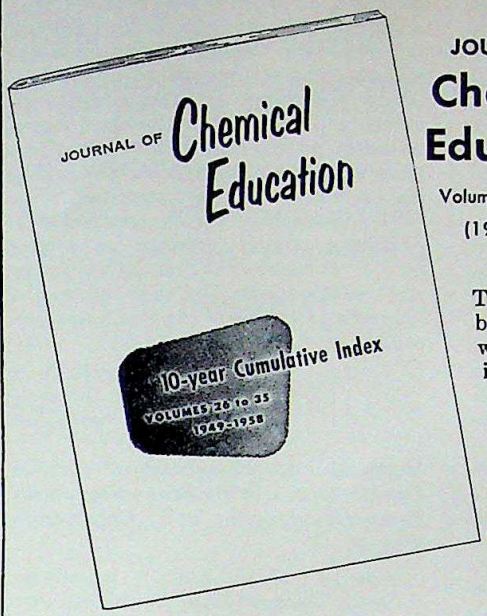
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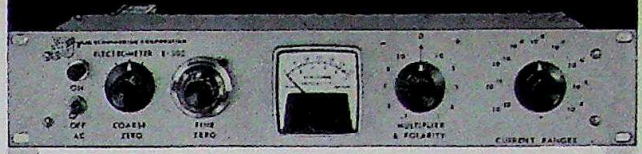
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the description of the various types of balances available.

The value of this book as a reference book on inorganic analytical chemistry is greatly enhanced by an excellent index. Methods for the determination of the various elements and anions are indexed under the name of the substance to be determined, and the method used is also given.

In the reviewer's opinion this book could well be the most useful single volume in the library of the analytical chemist.

FRANK J. WELCHER
Indiana University
Indianapolis

Hydroboration

Herbert C. Brown, Purdue University, Lafayette, Indiana. W. A. Benjamin, Inc., New York, 1962. xiii + 290 pp. Figs. and tables. 16 × 23.5 cm. $10.

This book is a critical review of the recently discovered reaction, hydroboration. Much of the information has appeared previously only in the form of brief communications to the editor, and thus is discussed in detail for the first time in the book. Since the reaction was discovered, and to a large degree, exploited, by Professor Brown and his group, it is particularly appropriate that he has taken the time and trouble to put all of the material together in a coherent fashion. The reaction, basically, the conversion of an olefin, *via* an organoborane, to an alcohol, promises to be useful for a wide variety of synthetic applications.

The book begins with an introductory survey of the reaction, and then in the following chapters, the history, scope, mechanism, and applications of the reaction to various types of olefins are considered in detail. The generous use of formulas and equations makes the material easy to understand, and it is well documented with references to the original literature. Comparisons of the hydroboration method with other reactions which accomplish the same end are made throughout. Unsolved problems and new areas for research are frequently mentioned. There is also considerable discussion of the chemistry of organoboranes and borohydrides.

By the use of this reaction, olefins, under mild conditions, can be converted to organoboranes, which can then be isomerized to other organoboranes. The organoboranes, again usually under mild conditions, can in turn be converted to alcohols, hydrocarbons, organometallics (such as dialkyl mercury compounds), more complex carbon structures, cyclopropanes, and olefins isomeric with the original one. The yields in general are high, the reaction is stereospecific, and applicable to a variety of olefins. For these reasons, it promises to rank with the handful of widely useful reactions in organic chemistry. Thus this book will be useful to every organic chemist faced with the problem of carrying out the reactions mentioned above.

The historical perspective with which this book is written also makes it valuable for advanced undergraduate and beginning graduate students, since they can readily see how the discovery of a new reaction (accidental, incidentally) can lead to a wide variety of new research problems. Professor Brown states that, surprisingly, he enjoyed writing this book, and this reviewer enjoyed reading it, and in fact, read it through in one sitting. The style is interesting, the chapters are short, and material is repeated where necessary, so that the reader does not have to refer back to previous chapters. The book is remarkably free from errors.

"Hydroboration" is recommended to practicing organic chemists as a good source of information on an important and useful reaction, and to students as an interesting example of the way a new area of chemistry can be developed.

HAROLD R. NACE
Brown University
Providence, Rhode Island

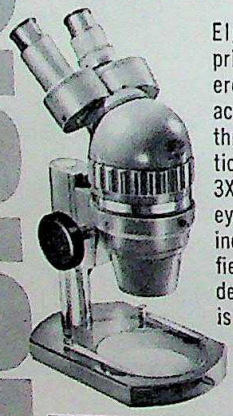
Methoden der Organischen Chemie. Band V/3: Halogenverbindungen: Fluorverbindungen und Chlorverbindungen.

Edited by *Eugen Müller*. 4th edition. Georg Thieme Verlag, Stuttgart, 1962. lxiv + 1217 pp. Figs. and tables. 18.5 × 26cm. 262 DM.

Daniel Boone, the great frontiersman, was once asked if he had ever been lost.

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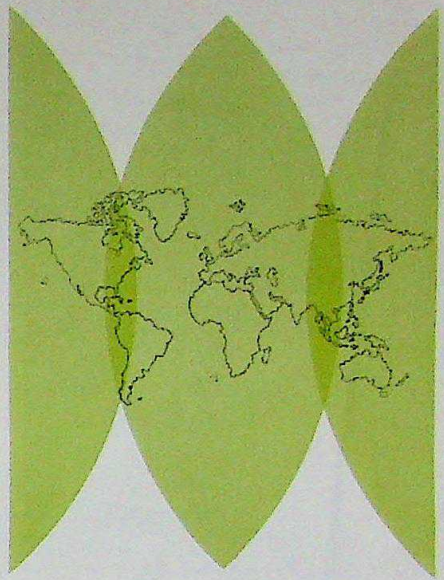
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The second major division (573 pp.) deals with the preparation of organic chlorides. Section I, the introduction, outlines the general features of laboratory work with the reagents and the products. Section II describes the preparation of chlorides through interaction of organic substances with free chlorine. Section III surveys the methods of synthesis which involve reagents containing chlorine. Sections IV through VI summarize the procedures involving condensation and degradation reactions leading to the formation of organic halides. Some variations of the elimination type have been surveyed in Band V/4, p. 718. The last part is an exceedingly useful tabular index (54 pp.) which lists the type of structure undergoing the reaction, the reagent, the kind of reaction involved, and the page numbers where specific examples are described.

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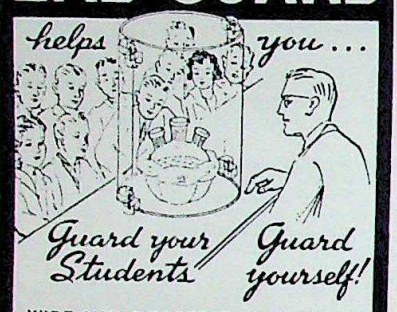
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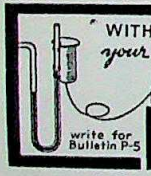
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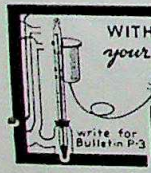


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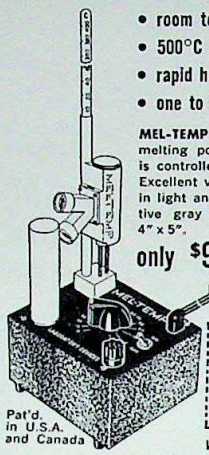


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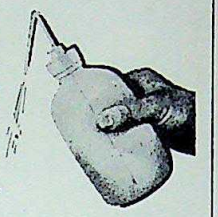
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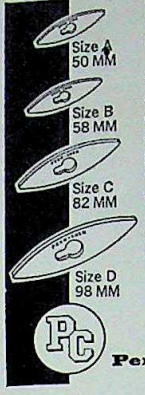
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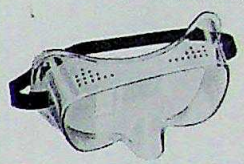
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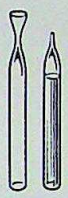


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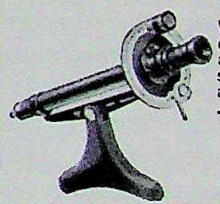
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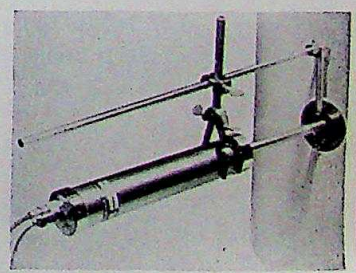
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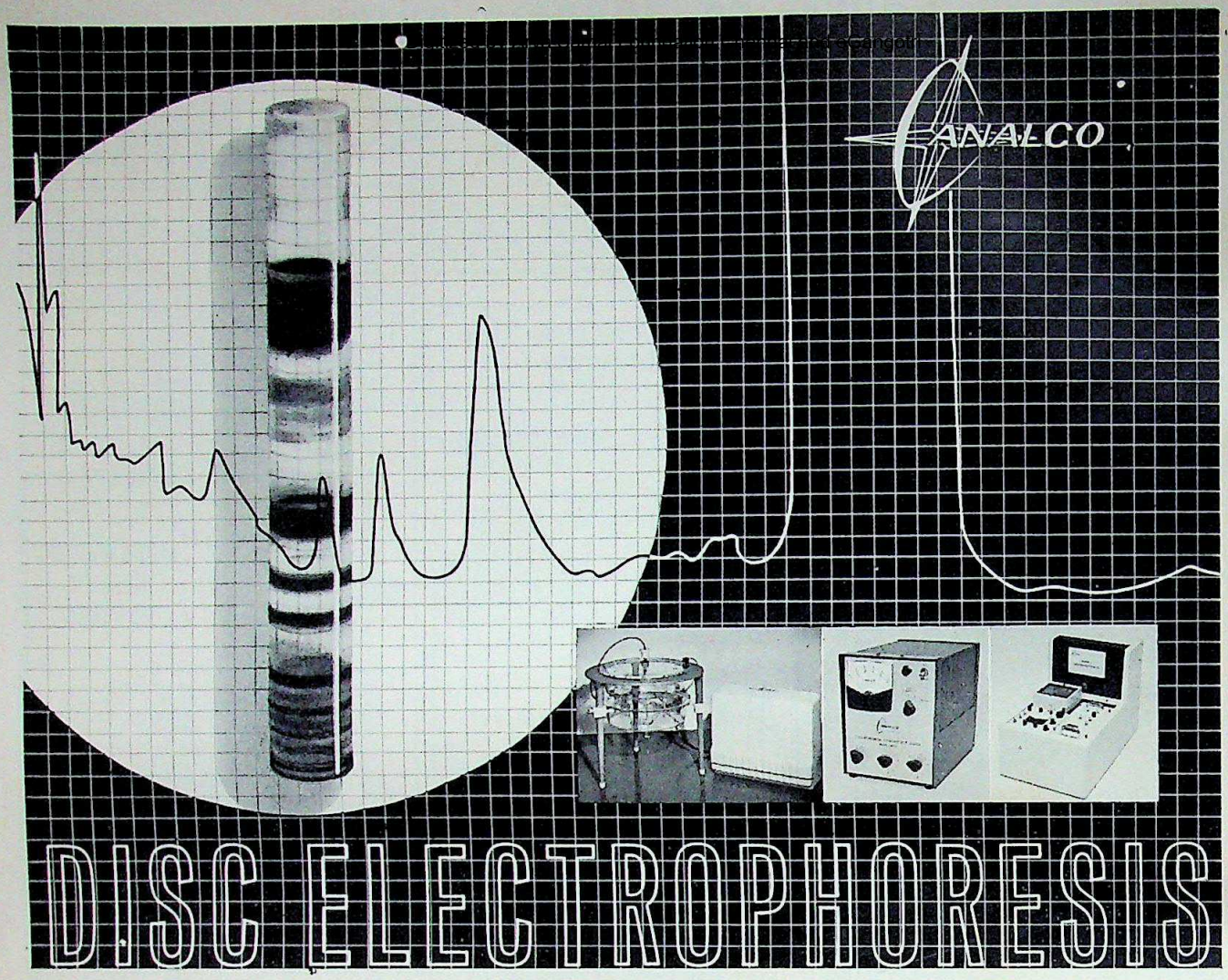
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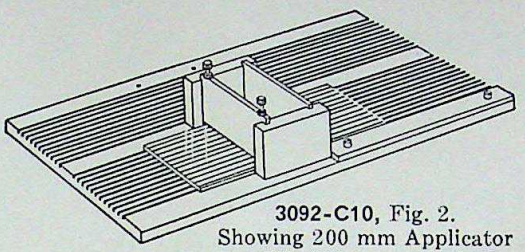
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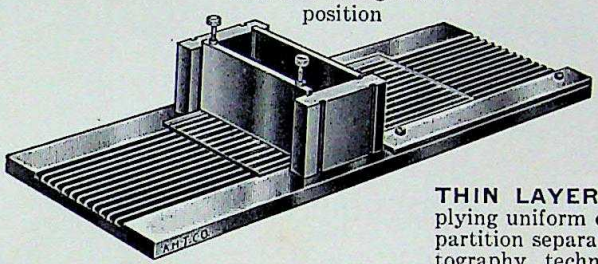
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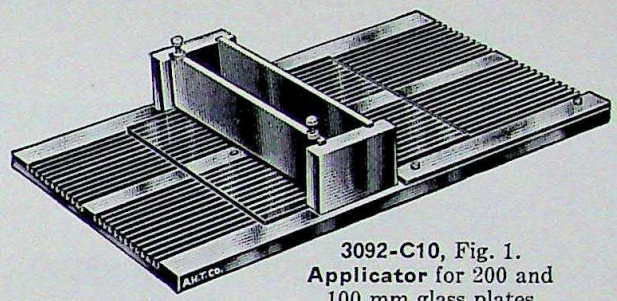
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3092-C10, Fig. 2. Showing 200 mm Applicator with 100 mm gates in position



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3092-C10, Fig. 1. **Applicator** for 200 and 100 mm glass plates

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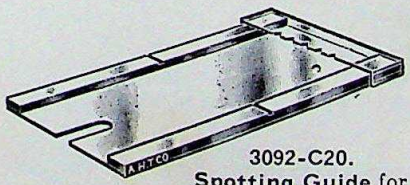
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Edited by **S. Z. LEWIN,** New York University, New York 3, N. Y.

These articles, most of which are to be contributed by guest authors, are intended to serve the readers of this JOURNAL *by calling attention to new developments in the theory, design, or availability of chemical laboratory instrumentation, or by presenting useful insights and explanations of topics that are of practical importance to those who use, or teach the use of, modern instrumentation and instrumental techniques.*

VI. Differential Thermal Analysis

Saul Gordon, *Department of Chemistry, Fairleigh Dickinson University*



Saul Gordon, Associate Professor of Chemistry and Vice-Chairman of the Chemistry Department, is at the Florham-Madison Campus of Fairleigh Dickinson University in Madison, New Jersey. A graduate of Ohio State University (B.A., 1946) and the University of Kentucky (M.S., 1946; Ph.D., 1951), he served successively as research chemist, group leader, Chief of the Basic Chemical Research Unit and Staff Specialist for Chemistry in the Pyrotechnics Laboratory at Picatinny Arsenal, Dover, N.J., prior to joining the faculty at F.D.U. in 1960. He was Chairman of the 1961 Eastern Analytical Symposium and is Director of the summer Thermoanalysis Institutes that have been established at the University. His teaching and thermoanalytical research are in analytical and physical chemistry.

When subjected to sufficiently high temperatures, virtually all substances will undergo physical and chemical changes ranging from simple changes in state to complete decomposition that can be studied by the various methods of thermoanalysis. During the course of these physicochemical reactions or phenomena, there will be concomitant sequential or overlapping changes in the enthalpy that lend themselves to a direct measurement by the technique of differential thermal analysis (DTA). As a thermoanalytical method, DTA may be used to characterize and experimentally evaluate a system by continuously measuring the changes in thermal properties due to physical and chemical reactions as they occur at elevated temperatures as a function of increasing temperature. The experimental approach is basically a rather simple modification of the more widely known method of thermal analysis used to evaluate phase diagrams, e.g., melting point versus composition for alloys or salt mixtures. Instead of using cooling curves for the single or multi-component samples, the system under investigation by DTA is heated to elevated temperatures at a predetermined rate of temperature rise. In addition, the temperature of prime interest is not the sample temperature per se, but the difference in temperature between the sample and a thermally inert reference compound which is heated concurrently with the sample under exactly the same conditions. This measurement is made by means of a pair of series-connected (electrically bucking) thermocouples, one of which is placed in the sample and the other in the reference material, as shown schematically in Figure 1. Both substances are contained in the same furnace block or otherwise heated environment so that they will experience a common heating cycle, generally a linear heating rate of 2–20°C per minute. If neither the sample nor the reference compound undergoes a thermal reaction over the temperature range involved, a continuous recording of the difference between the temperature of the sample and the reference or furnace temperature should result in a base-line which is parallel to the temperature axis. However, if the sample experiences an endothermal reaction, such as a first order crystalline transformation or even melting, these isothermal phenomena will cause the sample temperature to remain nominally constant while the temperature of the reference material continues to rise at the programed rate. Upon completion of the heat absorbing reaction the temperature of the sample, which has now lagged behind the reference temperature, will rapidly increase until the two substances are again at the same temperature. Further heating will cause both temperatures to rise at the same rate. A plot of the resulting difference in temperature as a function of temperature will produce a deflection from and subsequent return to the baseline, in the form of an endothermal band which is conventionally plotted in a downward direction. A similar effect is

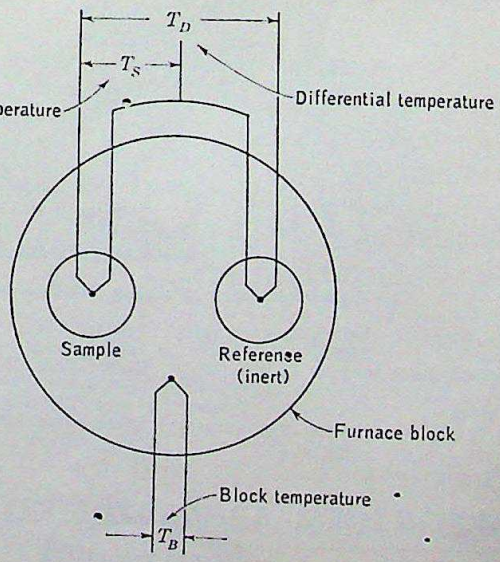


Figure 1. Schematic diagram for thermocouple assembly in typical DTA apparatus.

(*Continued on page A88*)

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obtained if the reaction is non-isothermal, as in the case of virtually all physical and chemical interactions, the specific nature of which will determine the shape of the

now exceeds that of the temperature-programed reference compound. When the reaction responsible for this evolution of heat has ceased, the sample will cool down to the temperature of the reference sample, from which point they will both continue to increase in temperature at the programed heating rate. A continuous

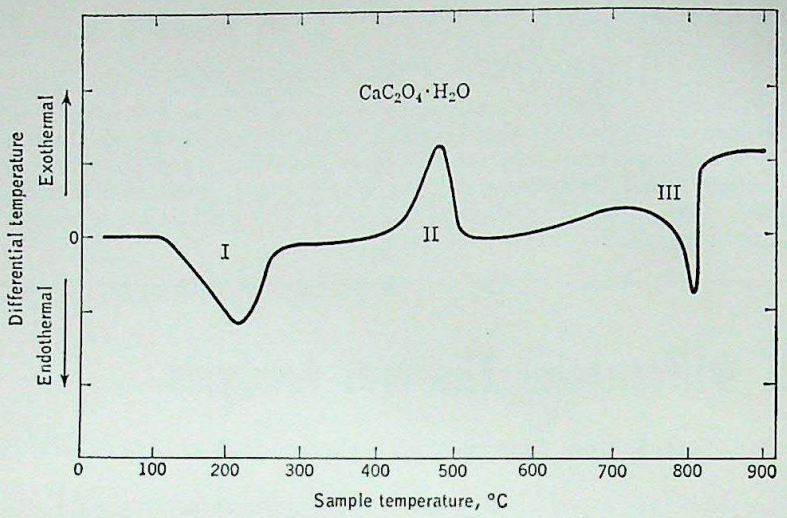


Figure 2. DTA thermogram for $CaC_2O_4.H_2O$ in an O_2 atmosphere; 8°C. per minute heating rate I, endothermal dehydration; II, exothermal oxidative degradation; III, endothermal decomposition.

respective endothermal band. Conversely, if the sample undergoes an exothermal reaction, the heat evolved will cause the temperature of the sample to increase more rapidly than that of the reference compound so that the sample temperature

recording of this difference in temperature as a function of sample or reference temperature will result in an exothermal band, conventionally plotted in an upward direction. The combination of

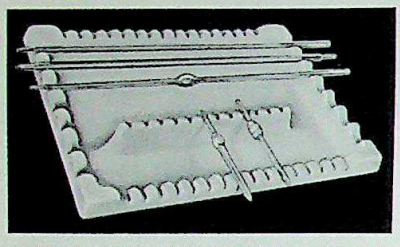
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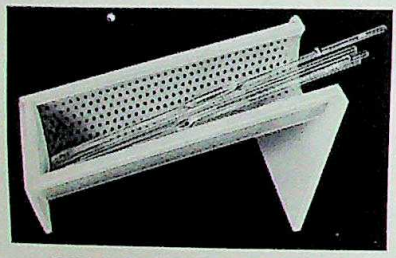
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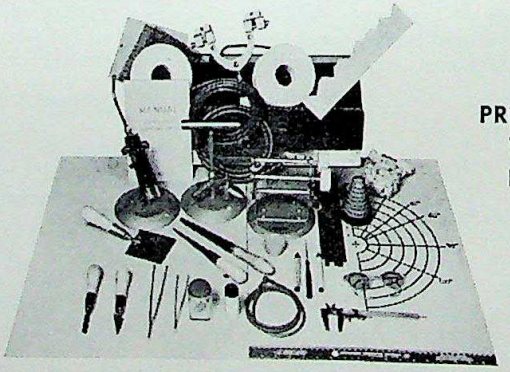
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endo- and exothermal bands obtained in DTA thermograms for any given sample represent "thermal spectra" that are very characteristic of any given system in that they indicate the temperatures and temperature ranges for fundamental changes in state, chemical composition and inter- or intra-molecular reactivity of the substance(s), as illustrated in Figure 2. These properties are, in turn, directly related to the thermochemistry and chemical kinetics of the physical or chemical atomic and molecular bonding which are inherent in properties and phenomena such as first order phase transitions, second order transitions and changes in state, such as fusion, boiling, and sublimation. This would also include adsorption and desorption, desolvation, decomposition, oxidation or reduction, solid state reaction, and all other reactions for which the corresponding enthalpic changes will produce measurable changes in the temperature of the sample relative to the reference substance. These are summarized in Table 1. Since non-isothermal reactions will have rates of reaction that vary as a function of the temperature, in accordance with the Arrhenius type of relationship ($K = Ae^{-E^*/RT}$), the thermal band shape will be determined largely by the activation energy, E^*.

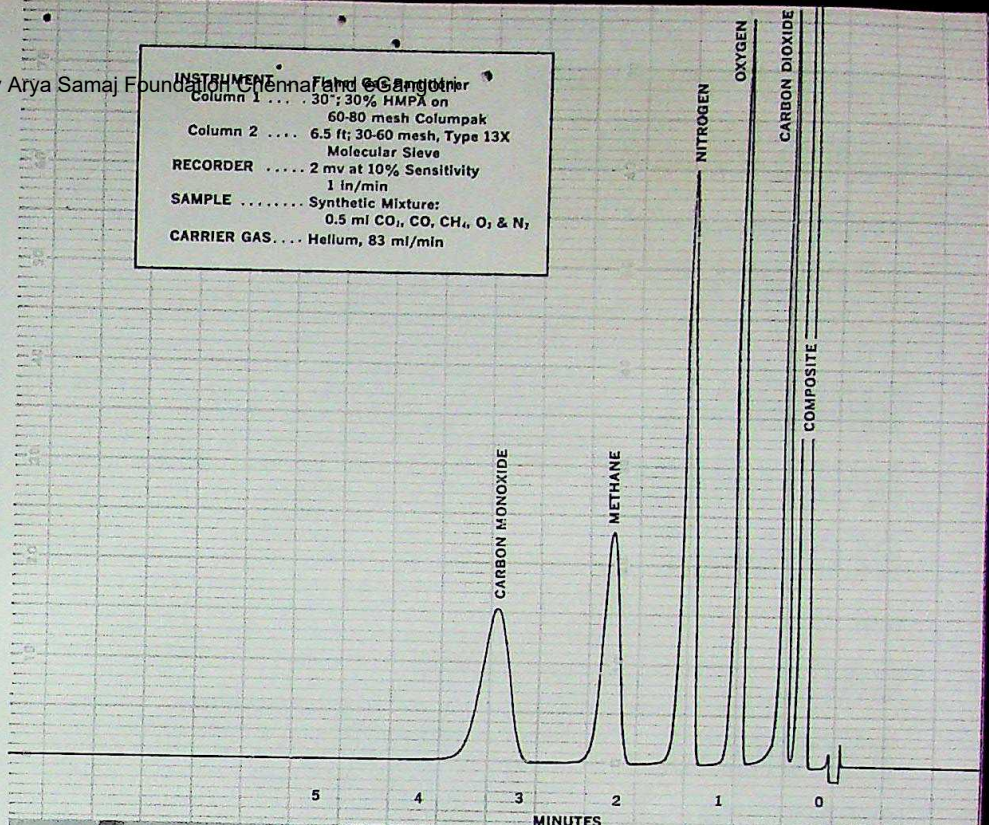
Other experimental factors such as the size, packing, geometry, and physicochemical history of the sample, electromechanical design of the instrumentation,

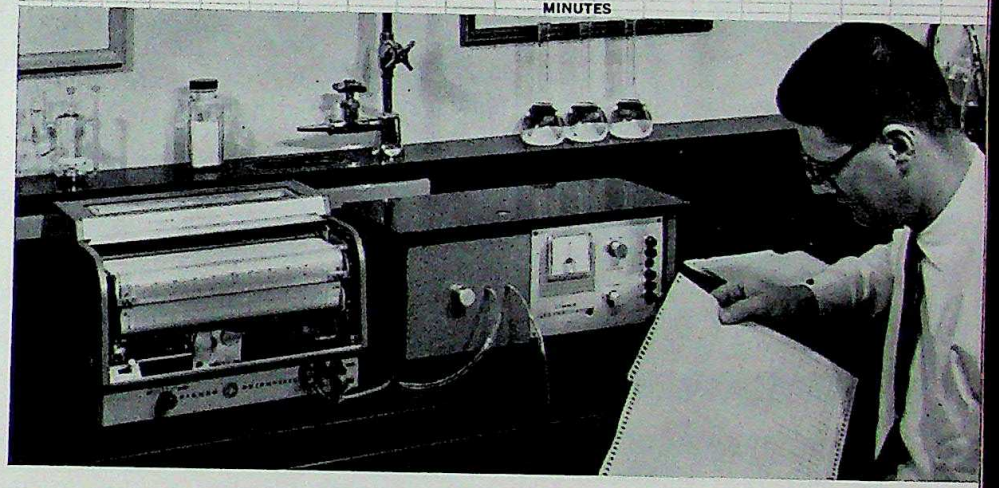
Table I. Physicochemical Phenomena and Reactions Amenable to Thermoanalytical Study by Differential Thermal Analysis

	Enthalpic Change	
	Endothermal	Exothermal
Physical		
Crystalline transition (1st order)	×	×
2nd order transition[a]	×	
Fusion	×	
Vaporization	×	
Sublimation	×	
Adsorption		×
Desorption	×	
Absorption	×	
Chemical		
Chemisorption		×
Desolvation	×	
Dehydration	×	
Decomposition	×	×
Oxidative degradation	×	
Oxidation in gaseous atmosphere	×	
Reduction in gaseous atmosphere	×	×
Redox reaction	×	×
Solid state reaction	×	×

[a]Often characterized by base-line shift due to change in specific heat.

gaseous environment, heating rate and the temperature (sample, reference or furnace) chosen for the abscissa will all affect the





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shape of the thermal bands obtained. The area under the band will be a function of the sample size, specific enthalpic change and specific heat, density, thermal conductivity and thermal diffusivity of the sample. These are experimental parameters that lend themselves to quantitative as well as qualitative applications and evaluations.

Although the technique of DTA has been applied very effectively and extensively by mineralogists, ceramicists, and metallurgists for many decades, it has only been during the past ten years that chemists have begun to utilize the method for diverse applications. To a great extent this has been the result of the recent development and commercial availability of the necessary temperature programing equipment and the high gain, low noise level dc amplifiers and sensitive dc recorders that are now so widely employed in the chemical laboratory. Additional impetus has come from the availability of thermobalances for thermogravimetric analyses that almost invariably provide the investigator with experimental data that can be evaluated adequately only with the complementary information derived from other thermoanalytical techniques, particularly DTA and more recently, effluence analysis. To this should be added the valuable information that may be derived from derivative thermoanalytical techniques. This has led several investigators to advocate the inclusion of DTA and other thermoanalytical experimentation in the undergraduate physical chemistry curriculum, for which easily constructed apparatus and specific experiments have been recommended.

During the past few years complete instrumentation packages for DTA studies have been developed and are now available from several domestic and foreign manufacturers. In virtually all of the apparatus designs there will be found the following modules or components: (*a*) sample and reference holder, (*b*) thermocouple assembly for measuring the sample and reference temperature and/or the block or furnace temperature, (*c*) furnace or other type of heating device, (*d*) suitable controls for regulating the pressure (vacuum and elevated pressures), and the composition of the gaseous environment in which the sample is being heated, either statically or with a controlled dynamically changing flow of gas through the sample, (*e*) temperature controller for obtaining fixed or variable heating rates, as well as constant temperatures for isothermal experiments, (*f*) stable, high-gain, low-noise dc amplifier for amplifying the temperature differences measured by the thermocouples, and (*g*) a recorder for plotting the difference in temperature as a function of sample, reference or furnace temperature, or of time.

In selecting an instrument for DTA studies, prime consideration must be given to experimental objectives and parameters, such as state and chemical com-

(*Continued on page A92*)

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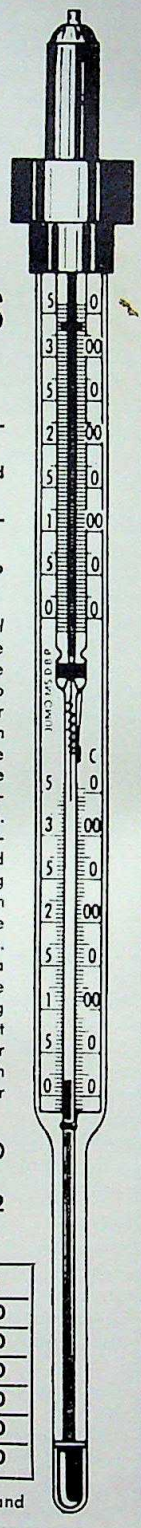
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DTA ** (differential thermal analysis) studies, on the other hand, measure enthalpic effects attending chemical or physical changes that occur in a sample as temperature is varied at a selected heating rate, but do not detect changes in weight. Complete thermoanalytical data are obtained only by utilizing both techniques.

The following curves illustrate a complete thermoanalytical investigation of calcium acetate monohydrate, including both DTA and TGA curves run in several types of atmosphere.

INTERPRETATION OF CURVES

The first reaction that occurs is the endothermal dehydration to the anhydrous salt that results in an endothermal band on the DTA curve between 200 and 250°C, and a corresponding weight loss plateau in the TGA curve at a comparable temperature region. The anhydrous salt remains stable up to temperatures of approximately 350 to 400°C, at which point endothermal decomposition reactions occur that are sensitive to the presence of oxygen in the environment. It is apparent from the TGA curve that the highly exothermal oxidative degradation that occurs in an oxygen atmosphere is completely different from the endothermal reaction occurring in argon, calcium carbonate being a product of the reaction in all cases.

In the presence of CO_2, the decomposition reaction appears to be similar to that occurring in argon. The thermal stability of the calcium carbonate, in an environment maintained at 1 atmosphere of CO_2, is increased to the extent that the decomposition to calcium oxide and CO_2 occurs at a temperature that is several hundred degrees higher.

This effect is also evidenced in the broadening of the endothermal band for the carbonate decomposition that is otherwise sharply peaked over a narrow temperature range in the CO_2 atmosphere.

INSTRUMENTATION

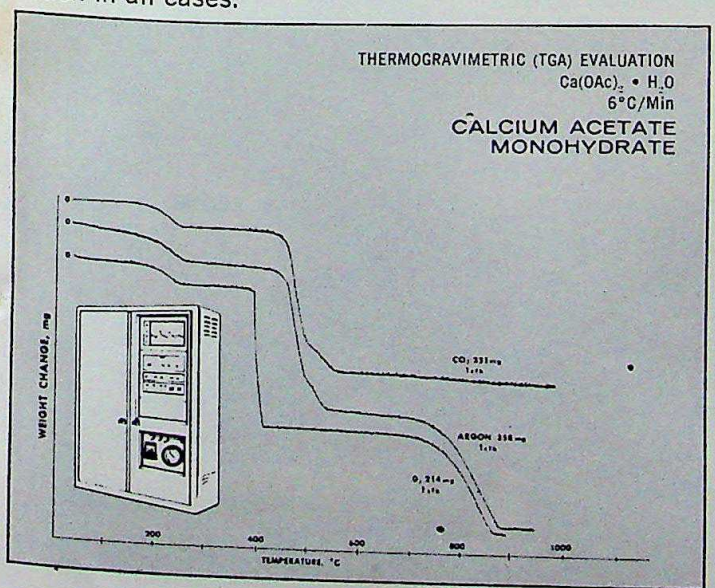
The instruments used to perform the thermoanalyses described above are Aminco's Thermo-Grav® for TGA, and the newly-introduced Thermoanalyzer for DTA work. The Thermo-Grav is an automatic recording thermobalance that measures changes in sample weight as a function of: (1) temperature programmed for a selected linear heating rate; or (2) time, at a constant temperature. Studies can be performed in vacuum or controlled atmospheres at temperatures to 1000°C.

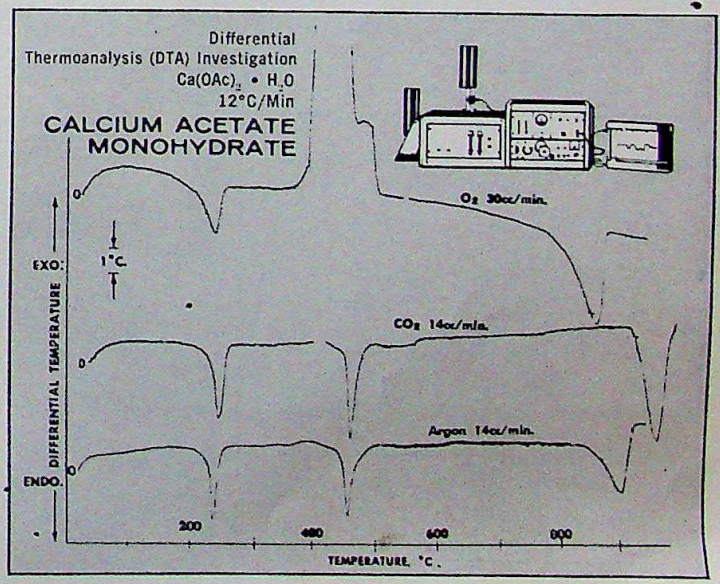
The Thermoanalyzer measures the temperature differential between a sample and a thermally-inert reference material, continuously recording this difference as a function of sample block temperature. Because sample temperature lags behind that of the inert reference during endothermal processes, and exceeds it when exothermal reactions occur, DTA curves consist of bands and peaks corresponding to the characteristic physicochemical reactions of the substance.

LITERATURE ON REQUEST

Aminco's Thermo-Grav® (TGA) is described in Bulletin 2328A-NK2.

The new Thermoanalyzer (DTA) is described in Bulletin 2380-NK2.





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AMINCO

American Instrument Co., Inc.

8030 Georgia Avenue, Silver Spring, Maryland

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ical and chemical reactions anticipated, the use of static versus dynamic gaseous atmospheres and pressure or vacuum requirements, need for effluence analysis of reaction products, upper and lower furnace temperature limits, variability of heating rates, and compatability of the sample and its reaction products with the materials of construction used in the apparatus.

American Instrument Co.

The Thermoanalyzer, shown in Figure 3, is a differential thermal analysis apparatus manufactured by the American Instrument Co., Silver Spring, Maryland ($4800), that utilizes a high temperature pressure-vacuum electric furnace based on a design developed and reported in the literature by W. Lodding and L. Hammell. A metal block with holes for the sample and reference is mounted on two single bore ceramic thermocouple insulators through which pass swaged thermo-

(*Continued on page A94*)

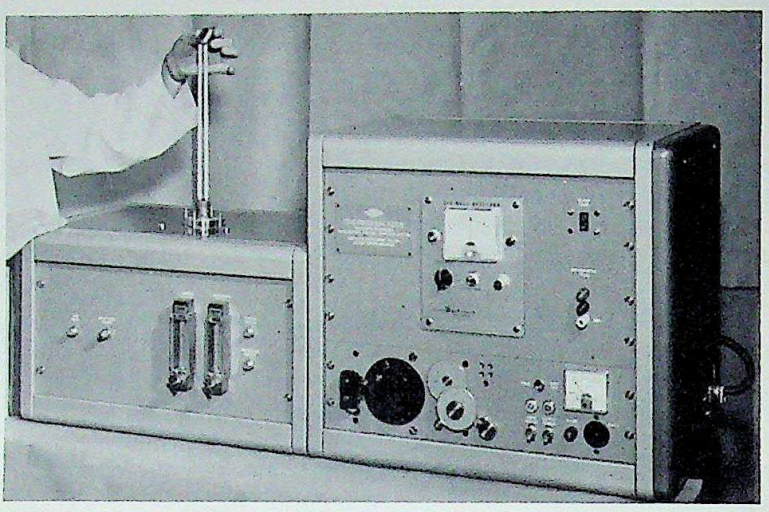
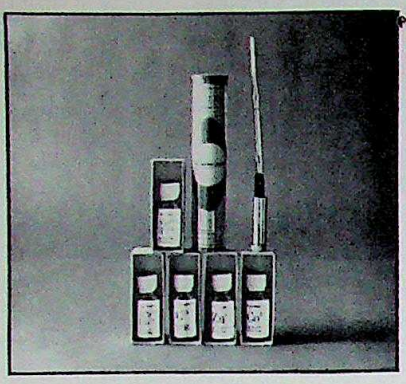


Figure 3. American Instrument Co. Thermoanalyzer.



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S-35 (Sulfuric Acid)	1	50	7.50
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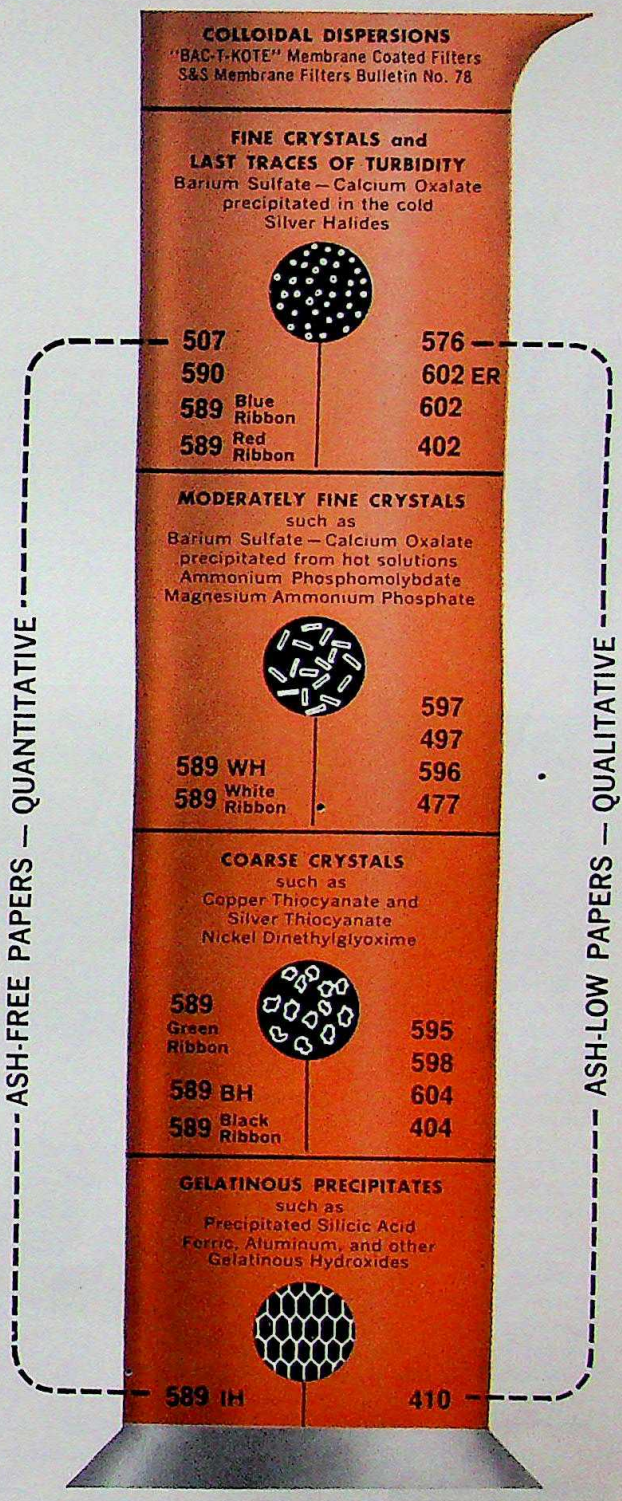
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adjusting the flowmeter needle valves, as indicated in Figure 4. This provides the means by which a uniform gaseous atmosphere can be maintained throughout the

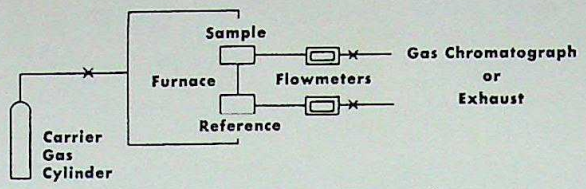


Figure 4. Flow Control System for Aminco Thermoanalyzer.

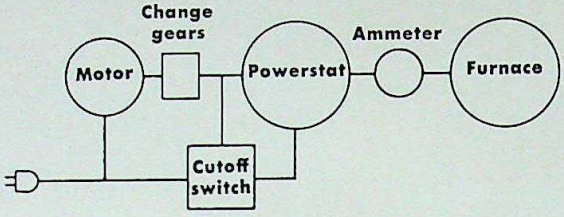


Figure 5. Furnace power programmer system in Aminco Thermoanalyzer.

couples that protrude through the block into the packed sample and reference. These thermocouples, with shielded or bare junctions, are used for measuring the temperature differentials and either the sample or reference temperature. A third thermocouple is available for insertion into the block for measuring block or furnace temperature. The thermocouple insulator assemblies are connected to the base in such a way that a dynamic flow of gas can be passed through the sample and reference during a DTA experiment at various pressures or under vacuum, by sample and also serves as the carrier for removing volatile reaction products and transporting them to external collecting devices or analytical instruments for concurrent or subsequent analysis. A kit consisting of another block and quartz or metal sample cups is available for studies of fusible samples that would otherwise melt and flow into the annular space between the thermocouple and the single-bore insulator. The cups are inserted into holes in this block and are seated on the thermocouples. A controlled flow of

(*Continued on page A96*)



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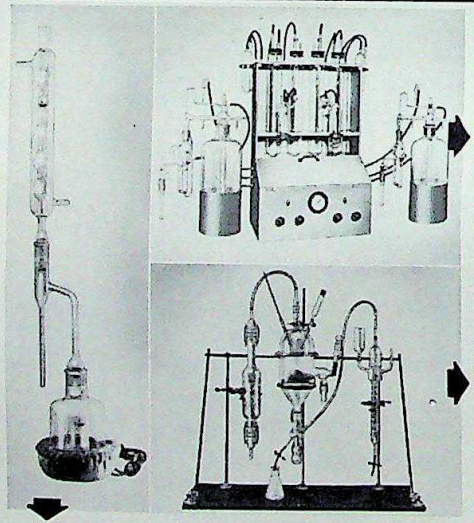
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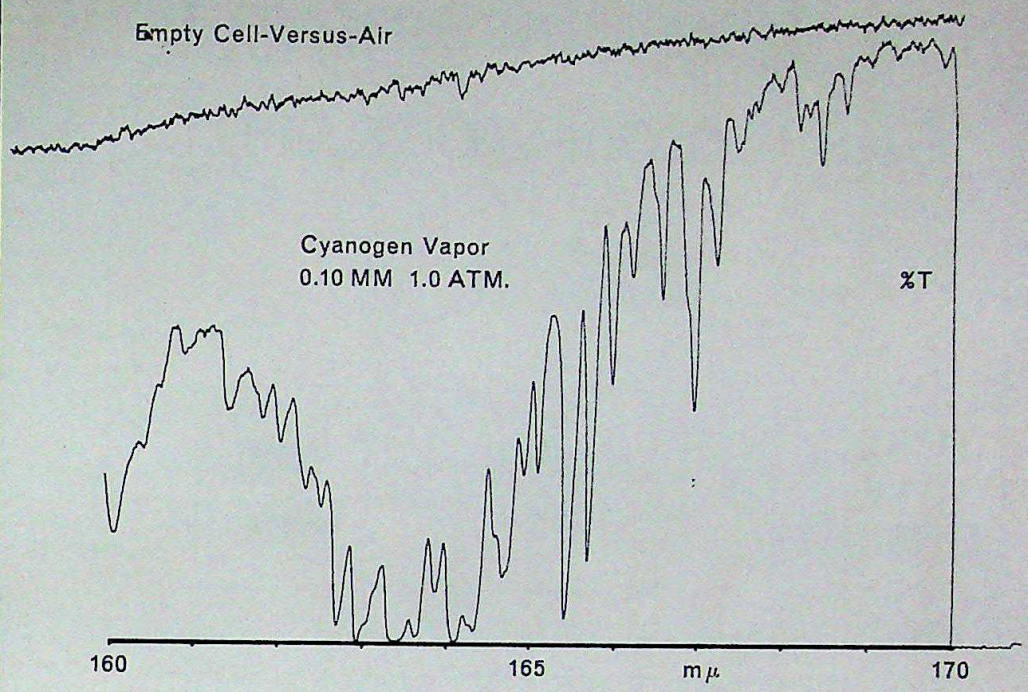


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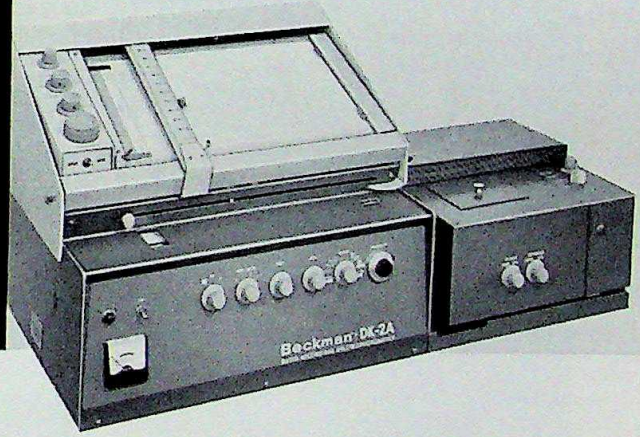
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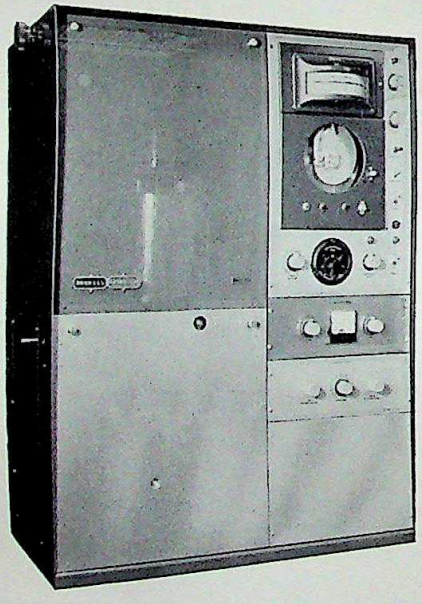
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gas may be passed through this assembly to surround the cup with the required inert or reactive gaseous environment and carry off the volatile reaction products for venting or analysis. Twin 1000°C resistance wound furnaces with removable radiation shields are provided for sequential analyses, thereby allowing the hot furnace to cool down for subsequent use during the following run. The required rate of temperature increase is obtained by linearly increasing the input voltage to the furnace with a motor-driven variable autotransformer, Figure 5. A wide choice of heating rates is obtained by the use of interchangeable gears, the standard values being 2, 4, 8, and 16°C per minute. Provision is made for the automatic cut-off or "hold" of furnace power at preset power levels with an adjustable limit switch. Amplification of the temperature differentials is provided by a stable dc amplifier with fixed levels of amplification ranging from 1 to 1000 in step ratios of 1, 2, 5, and 10. Although a recorder assembly is not provided with the basic instrument, the amplifier output can be conveniently connected to virtually any type of dc X-Y or strip chart laboratory recorders. Preprinted graph paper is available with a 0–1230°C chromel-alumel thermocouple x-axis suitable for use with X-Y recorders that have a sensitivity of 5 mv per inch or 50 mv full-scale, such as the Moseley or Houston recorders. The Thermoanalyzer is a thermoanalytical complement to the Aminco Thermograv, an automatic recording vacuum thermobalance for thermogravimetric analysis.

E. I. DuPont de Nemours

The DuPont 900 Differential Thermal Analyzer ($7500), Figure 6, available from the Instrument Products Division in Wilmington, Delaware, is a compact apparatus using disposable capillary melting point tubes of various diameters to contain

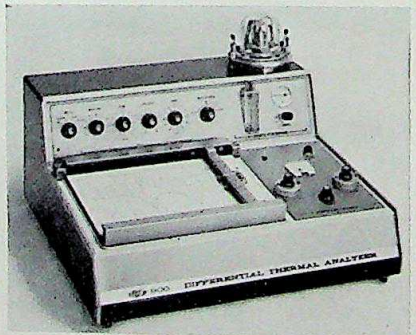


Figure 6. DuPont 900 Differential Thermal Analyzer.

micro or macrosize samples. These tubes are packed with sample and reference substances and inserted into a metal block that is heated by a replaceable resistance wire cartridge heater centrally located in the block, Figure 7. Simple plug-in thermocouples are in turn inserted into the contents of the two tubes. Additional

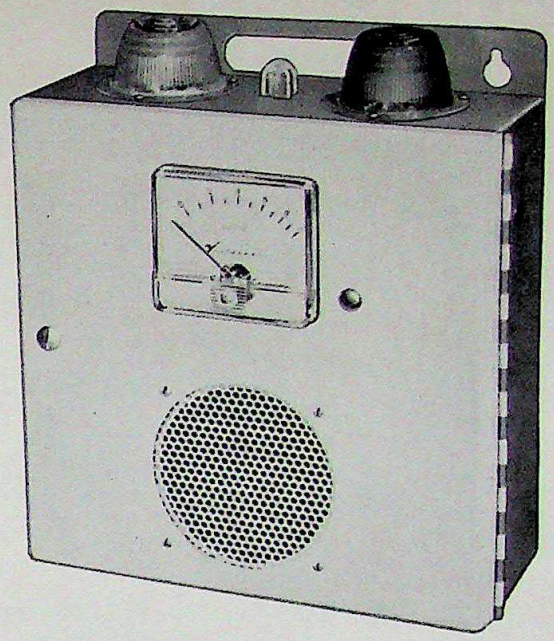
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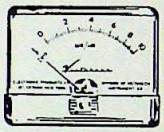
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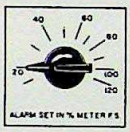
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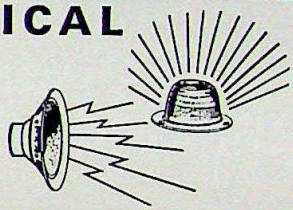
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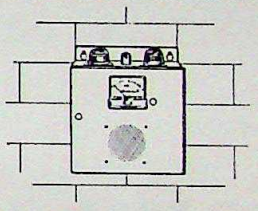
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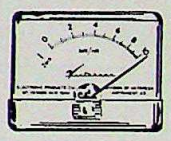
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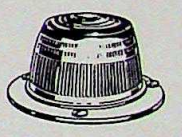
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determinations to be made with a series of samples either under vacuum or in an atmosphere of controlled composition

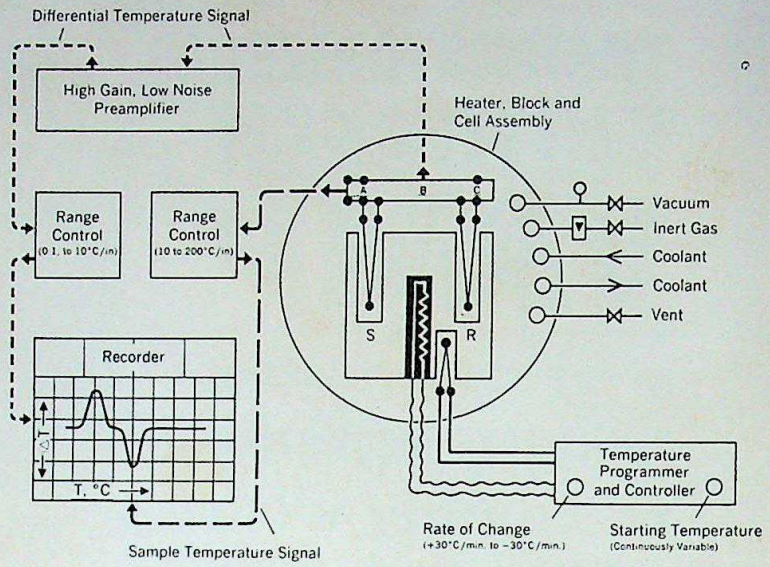


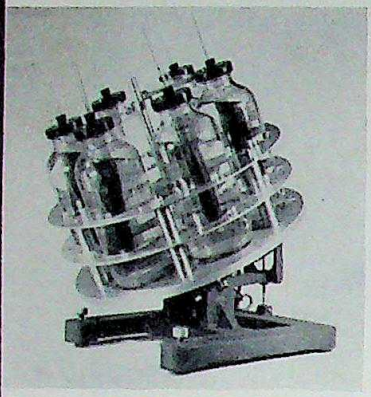
Figure 7. Schematic diagram showing construction of and circuitry for DuPont 900 Differential Thermal Analyzer.

block thermocouples are provided for temperature programing of the system and for recording the temperature difference as a function of block temperature. Provision is made for liquid nitrogen cooling of the analytical block assembly for runs involving temperatures below ambient. The sample cell assembly is enclosed by a small bell jar which provides a compact size for this assembly and allows rapid

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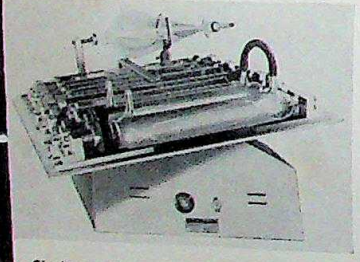
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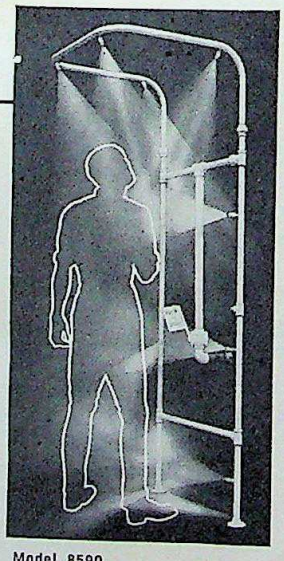
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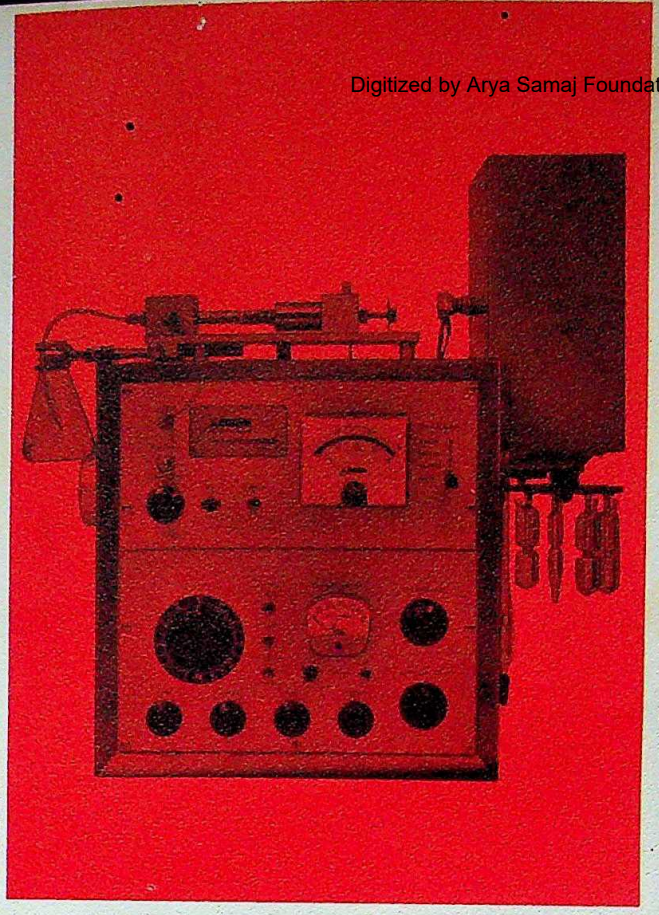
Model 8590
Multiple nozzle shower drenches victim from all angles.

Since 1909 HAWS **DRENCH SHOWERS**

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Autoprep Collector Bottle with special cap and vent valve which prevents sample contamination. Glass wool scrubber removes aerosols.

PREPARATIVE OR ANALYTICAL

WITH THE A-700 AUTOPREP

A good customer first brought to our attention that the Autoprep would also be useful as an analytical chromatograph. Since that time we have naturally made a big issue of this fact as it brings to focus the basic philosophy of this instrument .... preparative collection with analytical efficiency.

We have always found that if it can be separated on a packed analytical column it can be separated on the ⅜" Autoprep column.

The three basic modes of operation of this instrument are:

- **Automatic Preparative** — for many repeated operations to amass large samples for further use by the chemist. Automatic injection and collection with either programmed or isothermal temperature control.
- **Semi-Automatic Preparative** — for limited amount of feed material. The sample is injected by hand but is collected automatically by the rotating table.
- **Analytical** — for analysis without need of sample collection. The ⅜" preparative column may be used directly or exchanged with a ¼" or ⅛" analytical column. Injections are made by hand and the automatic collector may be used if desired. Programmed or isothermal temperature control can be elected.

ORDER

Aerograph Autoprep Model A-700, a fully automatic injecting and collecting preparative gas chromatograph with sequenced temperature programming from 25° to 350° C. Complete with 8 collector bottles, bubble flow meter, 20 ft. x ⅜" aluminum column and two injector needles for on-column or flash vaporized injections.

Model A-700 — complete including Brown Recorder with signal switch installed. Price **$3885.00**

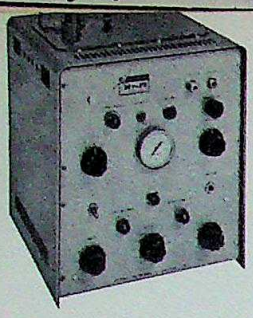
Model A-700 — as above, but without recorder. Price **$2885.00**

Send for Technical Data Bulletin on the Aerograph Autoprep 700.

AEROGRAPH FOR GAS CHROMATOGRAPHY

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AEROGRAPH A-600-B HY-FI — Manual Temperature Programming G.C. with Hydrogen Flame or Electron Capture detectors • gold-plated flame head • electrometer • standard accessories.

Price — $995.00



AEROGRAPH A-550-B HY-FI Oven — for Flame Ionization or Electron Capture Detectors • variably heated injector and column oven • stream splitter • detector base.

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AEROGRAPH A-500-B HY-FI Electrometer — line-operated • complete with Flame Ionization detector head • air pump • filter • standard accessories for gas and electrical connections.

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AEROGRAPH

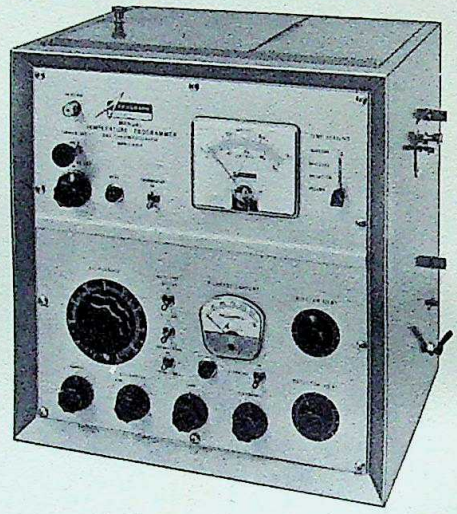
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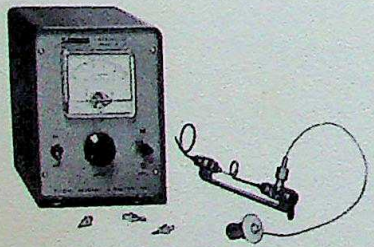
You can depend on us for your GC needs.

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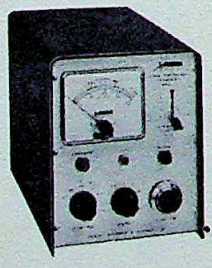
AEROGRAPH A-90-P — Manual Temperature Programing or Isothermal chromatograph with variable heat controls for: column oven (400°C), detector, collector and injector. Built-in 20V DC transistorized power supply • 4-filament detector • efficient sample collection system.

Price — $1085.00



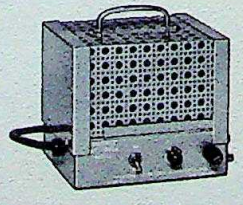
AEROGRAPH A-425 Pyrolysis Unit — thermally decomposes non-volatile materials for degradation pattern study. With three platinum pyrolysis coils • pyrolysis chamber • plumbing for connection to HY-FI.

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Price — $685.00



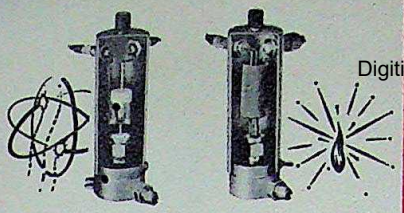
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AEROGRAPH Flame and Electron Capture Detectors — Interchangeable on standard base • for use with the HY-FI and HY-FI Oven.

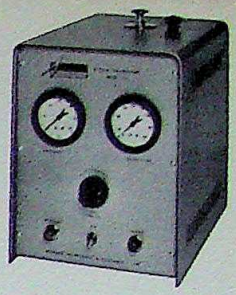
Price — F.I.D. complete with quartz tip $75.00

Price — E.C.D. complete with Tritium source $260.00



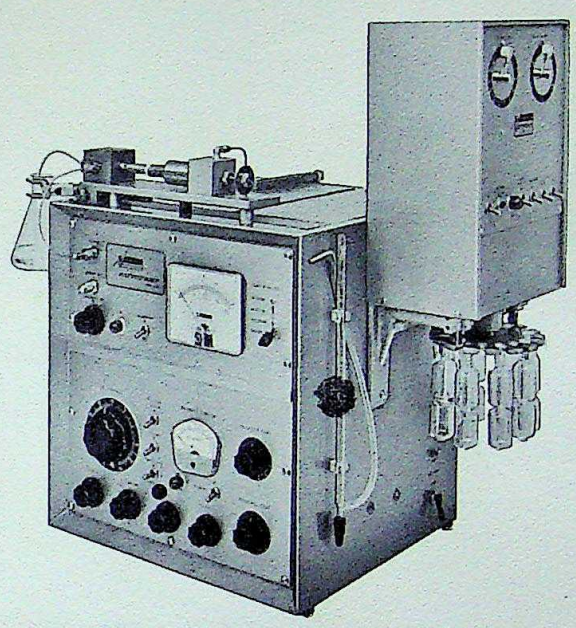
AEROGRAPH A-650 Hydrogen Generator — with filtered air supply • direct reading meter • controls • fittings for hydrogen and air. Used with Flame Detector.

Price — $295.00



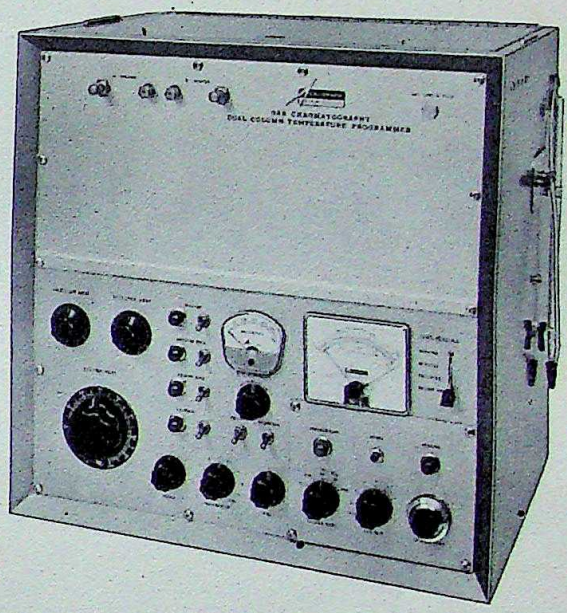
AEROGRAPH A-675 Steam Generator — supplies clean, dry steam for use as a carrier gas. Controlled pressure 0 to 50 lbs. • controlled temperature 0 to 150°C.

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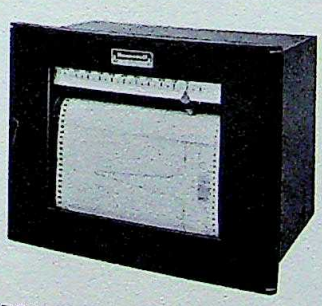
AEROGRAPH A-700 Autoprep — a fully automatic sample injecting and collecting gas chromatograph • automatic temperature programming from 0 to 400°C. Automatic collector holds 8 collector bottles with waste position between each.

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AEROGRAPH A-350-B — Dual Column Gas Chromatograph • ultra-sensitive with four-filament detector • double injector • automatic linear temperature programmer. Built-in 20 volt solid-state power supply • differential flow controllers on each column.

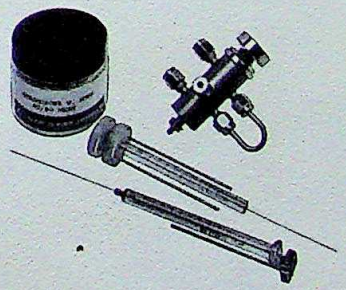
Price — $1995.00



RECORDERS — Brown, Class 15 • and Leeds & Northrup Speedomax H recorders o 1 mv and 1 sec full span. Carried in stock for immediate delivery.

Price — Brown Class 15 $1000.00

L & N Speedomax H $590.00



AEROGRAPH ACCESSORIES — A complete line of G.C. accessories including columns • supports • substrates • syringes • tubing • fittings • flow controllers • reductiton gauges • gaskets • integrators. See Aerograph G.C. Accessories Catalog.



AEROGRAPH PUBLICATIONS — Research Notes — Instrument Catalog • Accessories Catalog • Previews and Reviews • and Pesticide Bulletin • are mailed regularly to keep you informed on the latest G.C. developments.

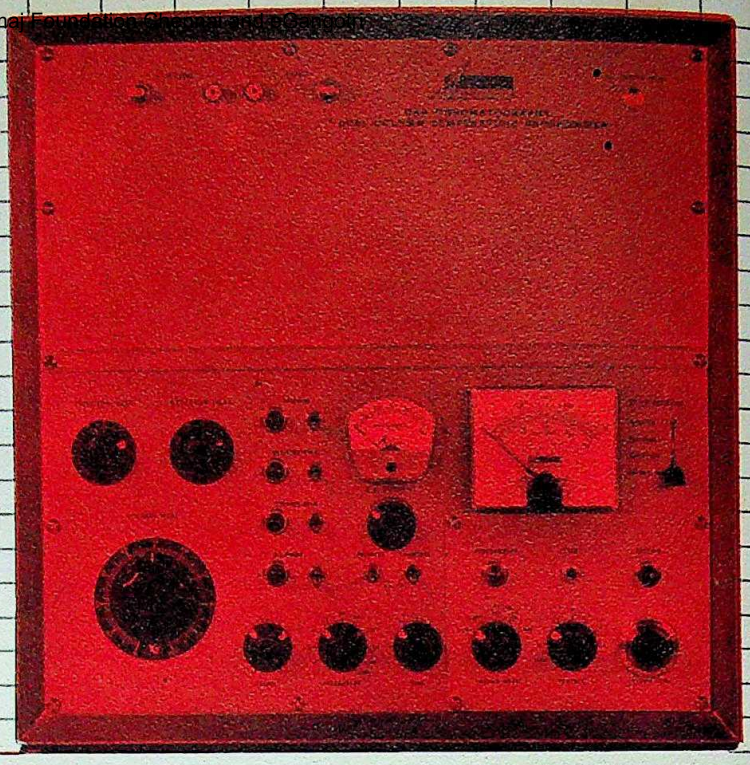
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THE AEROGRAPH A-350

WITH DUAL COLUMN SYSTEM AND LINEAR TEMPERATURE PROGRAMMING

People tell us that the Aerograph A-350-B is quite a gas chromatograph. It was the first commercial dual-column linear-temperature programming instrument, and has found a happy home in many of the great industrial laboratories.

Recently the A-350-B has been gone over with a fine tooth comb and some improvements have been made. A new 20 volt power supply, with increased range and extreme stability has been added. Long, tapered, micro-control needle valves in conjunction with the effective Moore Flow Controllers give constant carrier gas flow in both columns.

The A-350-B also gives such bonus features as on-column or flash-vaporizing injections; excellent means for sample collection; and low-mass oven for rapid, thermal change.

Above — The beautiful separation of Fatty Acid methyl esters was made on a 5' x 1/4" Silicone SF-96 column, matched by a similar column. The sensitivity was maximum, yet note the rock stability of the base line as the temperature was programmed from 70° to 250°C at 6°C/min.

Remember, with this chromatograph you are controlling the oven temperature with a platinum resistance bulb known to be one of the most accurate and linear means of temperature measurement.

The many repeat orders from people who know, give us confidence in recommending this superlative instrument to you. Write for further details and request special booklet on A-350-B Model Traces.

ORDER — Aerograph Model A-350-B, dual control linear temperature programming gas chromatograph with automatic linear temperature programmer, built-in 20 volt transistorized power supply and differential flow controllers. Power requirement 115 volt, 50/60 cycles.

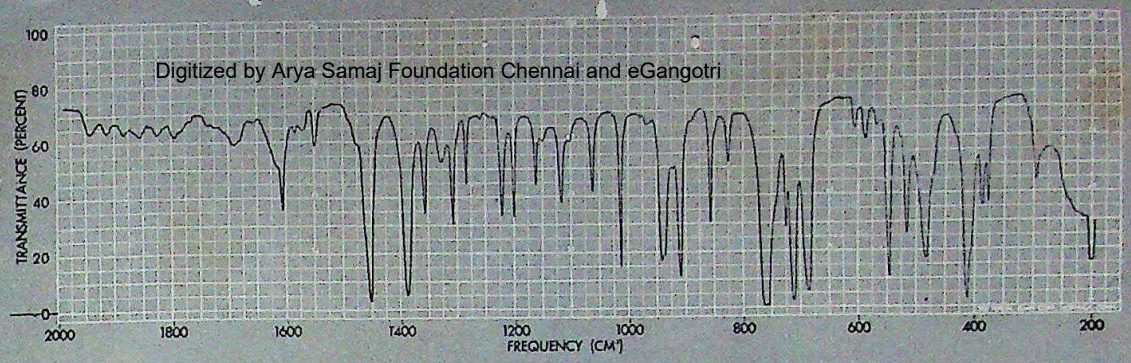
Accessories included: 10 lamba Hamilton Syringe, 24 injector gaskets, 12 collector gaskets, 2 five foot, s.s. matched columns, bubble flow meter, copper carrier gas line.

Price **$1995.00**

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This spectrum of indene and indene–camphor–cyclohexanone was recorded in 16 minutes through use of Model 421's long-wavelength grating interchange.

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Both interchanges give you true *grating* resolution—plus the Model 421's top-efficiency f/4.5 optical system that scans faster and handles samples smaller than any comparable instrument. An integral automatic speed suppression system guarantees accurate spectra in minimum time, adding to *your* working efficiency.

Get the whole story on what the Model 421—and its accessories—can do in your own applications. Write today for the new Model 421 brochure. The address: Instrument Division, Perkin-Elmer Corporation, 870 Main Avenue, Norwalk, Connecticut.



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perature cut-off or for cycling between any selected high and low temperature limits. A high gain, low noise solid-state dc amplifier is used in conjunction with a built-in X-Y recorder to continuously plot the thermograms at various sensitivities ranging from 4 to 400 μv per inch, corresponding to 0.1 to 10°C per inch with chromel-alumel thermocouples, for the temperature differential axis; and 0.4 to 8 mv per inch, or 10 to 200°C per inch for the temperature axis. The ink-pen plot may be made on preprinted millivolt or temperature scaled paper. An optional base-line compensation kit is available for providing electronic compensation for the base-line drift normally associated with improperly matched sample and reference substances.

Eberbach Corp.

The first commercially available DTA apparatus seems to have been the portable unit which is manufactured by Eberbach Corp., Ann Arbor, Michigan ($580), Figure 8. This unit was originally designed by R. A. Nelson and constructed in the Bureau of Plant Industry and Soils for widespread use by geologists in the U. S. Geological Survey in their field evaluations of various minerals and soils. The samples and reference substance are packed into three crucible cells, each of which is fitted with thermocouple assemblies for measuring the temperature differences by means of a pair of series-connected thermocouples which are connected to a sensitive galvanometer, and a third thermocouple for measuring the furnace temperature by connecting it to the built-in pyrometer. Each of the three stations is used in sequence by placing the furnace over the crucible and connecting it to a 115 v ac or dc source. The heating rate, which is not programed, is just the non-linear rate at which the furnace will heat up when either full line voltage or a rheostat-reduced power level is applied. During the course of this heating cycle the operator reads the two meters at arbitrarily chosen furnace temperature intervals, e.g., every 20 degrees, and manually records the data for subsequent plotting. At the end of the run the furnace is allowed

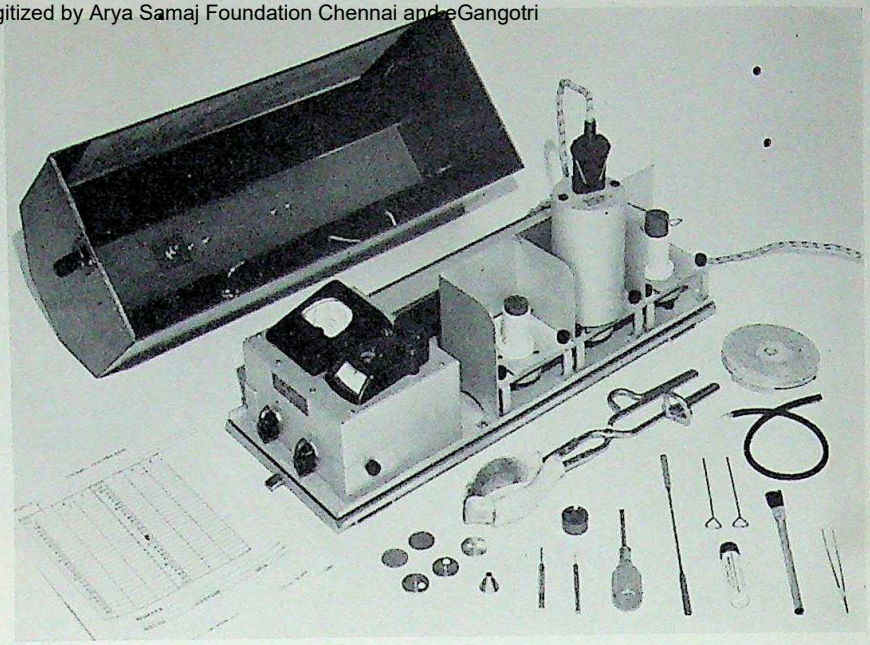
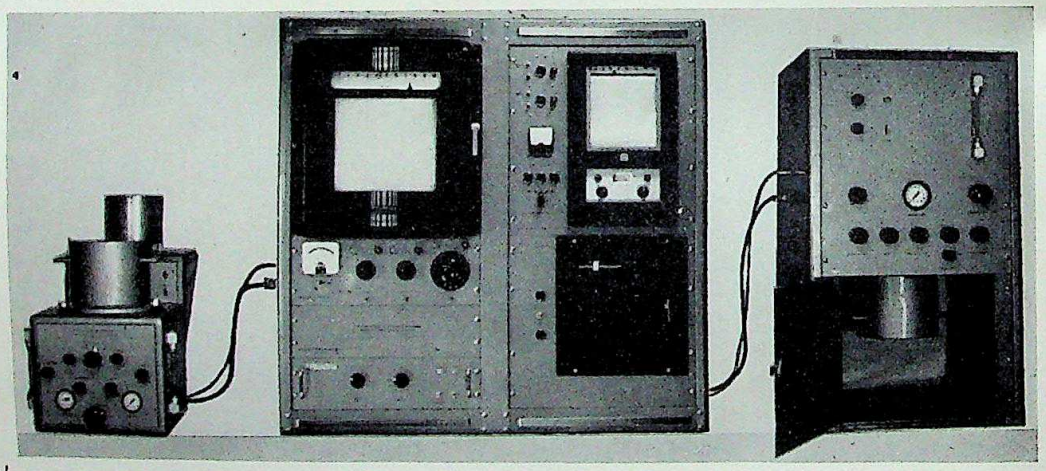


Figure 8. Eberbach Corp. Portable DTA apparatus.

(*Continued on page A106*)

DTA + TGA
+
Effluent
Gas Analysis

SIMULTANEOUS
DTA + G.C.



MODEL DTA—GS—2
Differential Thermal Analysis Pressure Chamber Assembly. Dynamic gas principle. Quick-interchange sample holders for powders, liquids, and simultaneous gas effluent analysis plus DTA. Pressures to 100 psia and vacuum to 10^{-4} mm Hg. Temperature range from —150°C to +1400°C.

MODEL DTA—JAC
Control Cabinet for DTA & TGA or DTA only. Twelve exact temperature rates from 0.4°C to 25°C per minute. Automatic rise-hold and rise-cool for temperature. Switch for using any instrument combination. Two-pen recorder for simultaneous recording of DTA and effluent gas analysis.

MODEL TGA—2
Thermogravimetric Analysis Pressure Chamber and Control Assembly. Pressure to 100 psia and vacuum to 10^{-2} mm Hg. Dynamic gas principle. Ranges: 20mg, 100mg, 200mg, and 500mg, of weight change for full scale of recorder. Samples up to 2.000 gm. No drift, no noise. Temperature to 1400°C.

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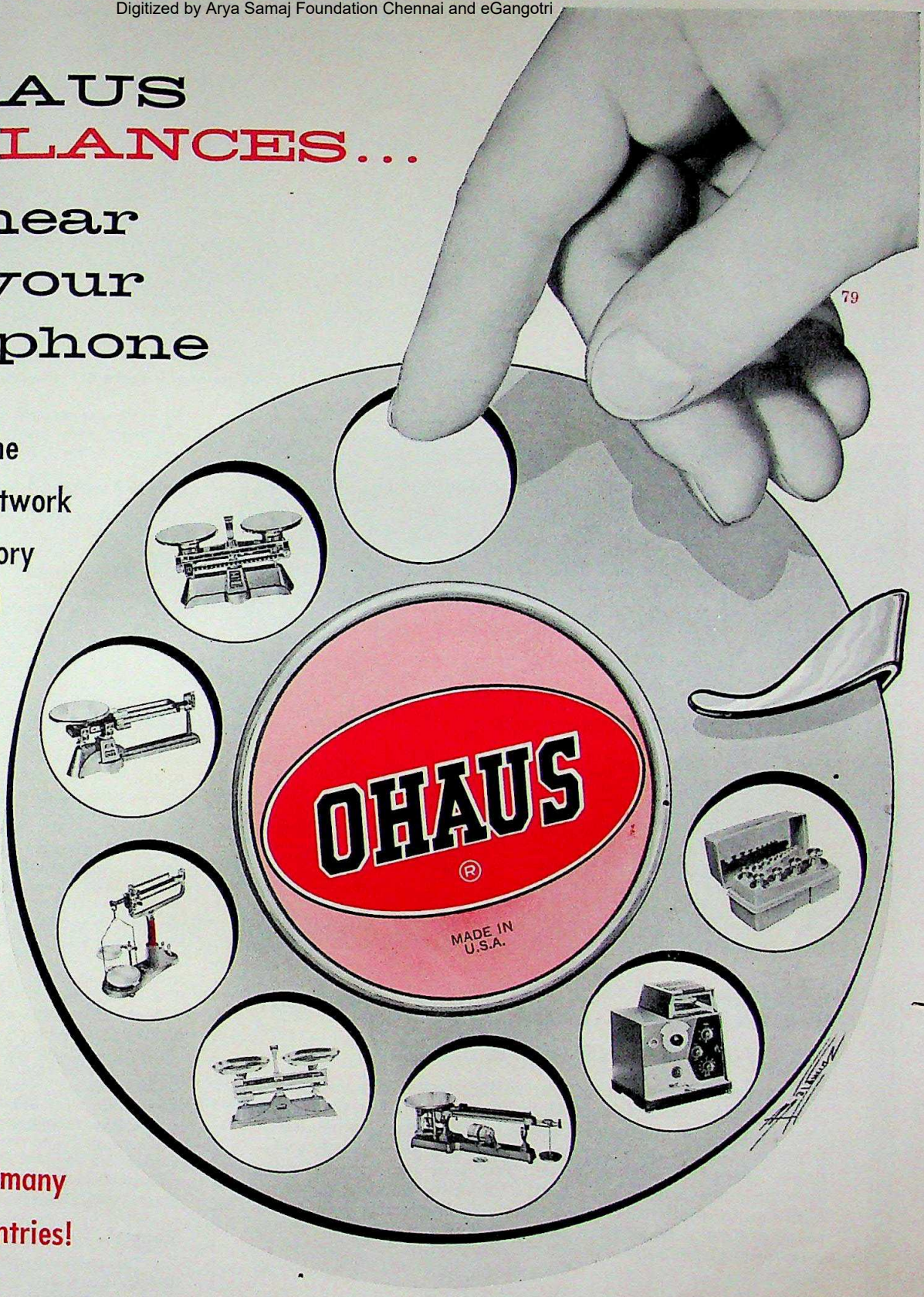
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to cool down to a suitable temperature, which may be well above ambient, and is placed over the second crucible for the next run. The same procedure is repeated for the third crucible. By calibrating the instrument with samples having known enthalpic changes and restricting the measurements to temperature ranges in which significant thermal bands appear if the particular mineral or soil component is present, very useful qualitative and semiquantitative data can be obtained.

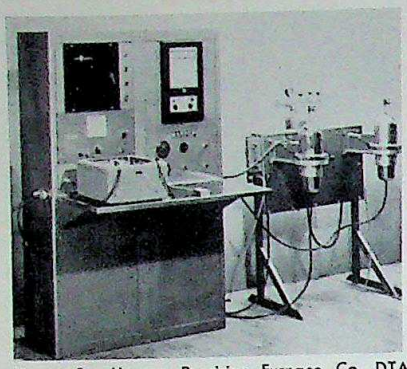


Figure 9. Harrop Precision Furnace Co. DTA apparatus.

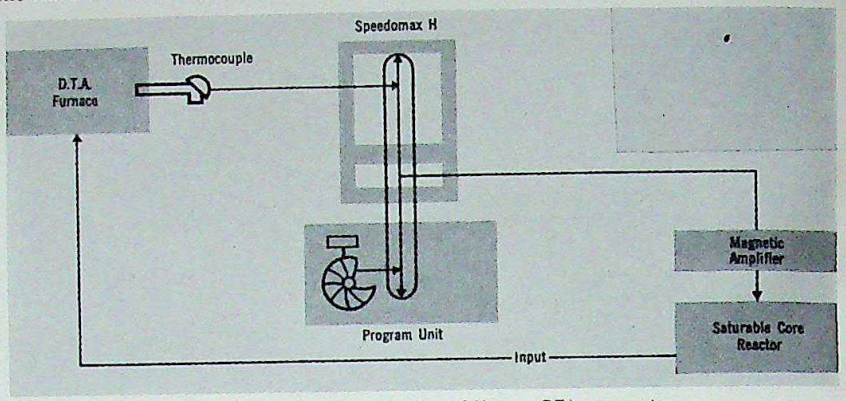


Figure 10. Schematic diagram showing operation of Harrop DTA apparatus.

Harrop Precision Furnace Co.

The Harrop DTA apparatus, Figure 9, is manufactured in Columbus, Ohio. It is essentially a custom-built unit comprised of various component options combined into one assembly in accordance with the needs of the purchaser. Major modules are the control panel and basic wiring cabinet for the primary instrument power with a magnetic amplifier and current limiter for a 1 kva saturable reactor through which the furnace is controlled, and space as well as input connectors for the temperature programer, high gain dc amplifier, and X-Y recorder, Figure 10. A manifold and associated flowmeters, valves, and connectors are provided for experiments in controlled gaseous atmospheres at ambient or elevated pressures or under vacuum. The temperature programing system is a Leeds & Northrup 3-mode current adjusting control system with strip chart recorder using a motor-driven cam and interchangeable gears for obtaining a wide choice of heating as well as cooling rates, Figure 10. By using a zero-centered 10 mv dc recorder with the L & N indicating preamplifier, differential temperature ranges equivalent to ± 25 to 1000 μv may be obtained. A modified Houston X-Y recorder is offered for plotting differential temperature as a function of temperature. Platinum or nichrome wire wound furnaces are available for temperature ranges up to 1400 or 1100°C, respectively. The recording and control systems are designed for optional use with a thermobalance for complementary thermogravimetric studies.

Robert L. Stone Co.

DTA apparatus available from the Robert L. Stone Co. of Austin, Texas, consists of various combinations of several basic modules covering a wide range of prices and capabilities. Basic to all models is a furnace platform to which is added (a) any one of several interchangeable sample holders for solids or liquids; single or multiple samples; sample holders and specimen cups fabricated from various

(Continued on page A110)



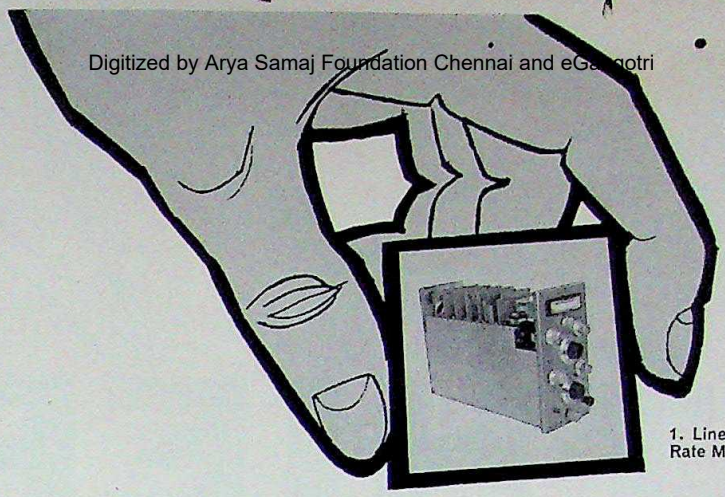
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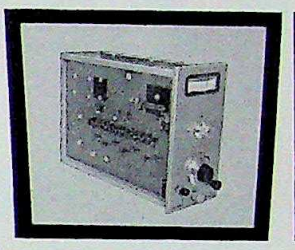
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First with polyolefins for corrosion-resistant drainline systems.
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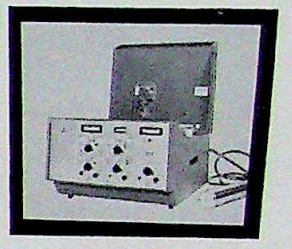
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1. Linear-Log Count Rate Meter

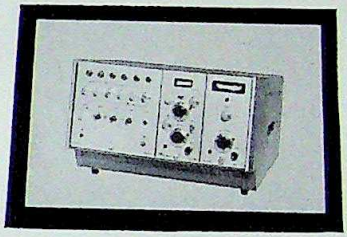


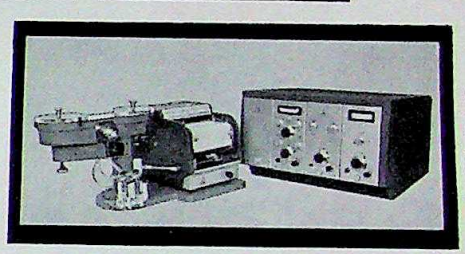
2. High Voltage Power Supply



3. Blank Panel, Linear Count Rate Meter, Single Channel Analyzer, High Voltage Power Supply

4. Printing Scaler-Timer, Single Channel Analyzer High Voltage Power Supply





5. Chromatograph Scanner, Linear-Log Count Rate Meter, Linear Amplifier, High Voltage Power Supply

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PROGRESS REPORT: Start with a simple module (linear amplifier, single channel analyzer, or count ratemeter) add the power supply, detector and read-out device and you have the simplest of spectrometer systems. As funds permit, you can add another module (quickly substituted for the blank panel in the chassis) and perform the additional experiments you desire.

When you are ready for automatic scaling or counting of your spectra, the double module scaler-timer can be added. You can simultaneously add a print-out facility to integrate the total energy under a peak automatically or to record this energy as a digital output. Depending upon the selection of the read-out device, simultaneous chart recording is also possible.

The widest possible choice of input and output devices is available. G-M or Scintillation detectors can be accommodated by simply reversing the printed circuit card in one of the modules. More advanced devices for automatic sample counting, gas flow counting, or paper chromatograph counting also are available.

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metals and alloys for use in a variety of atmospheres and with corrosive samples; and for simultaneous DTA and effluence gas analysis (EGA); (*b*) a furnace for either 1100 or 1400°C operation; and (*c*) a pressure top for extending the pressure range from atmospheric to vacuum or elevated pressures up to 100 psi. Additional accessories provide for dynamic cycling of the gaseous atmosphere either through or around the sample, and, with the vapor generator and preheater coils, it is feasible to use a condensable substance such as steam for the dynamic gas. The schematic diagram in Figure 11 shows the construction and operation of the furnace platform assembly with dynamic gas flow system, thermocouple arrangements, furnace, and pressure chamber. Several recorder-controller assembly models are available with temperature programer and strip chart recorders for both differential temperature and reference temperature, the latter with a built-in device for marking the thermograms with pips at 100°C intervals. The types of programers available range from the simpler modified West JSB-1 motor-driven cam actuated pyrometer with a nominal 10°C per minute heating rate, to the more sophisticated Leeds & Northrup with CAT that provides twelve exact heating rates from 0.4 to 25°C per minute and the automatic temperature limit switch functions of rise-off, rise-hold, and rise-cool. The high gain dc amplifier has an adjustable gain ranging from 5 to 4000 μv, or with the standard Pt-Pt, 10% Rh thermocouple, a full-scale differential temperature of 0.5 to 350°C. With the two-pen recorder and an additional amplifier, two samples may be run concurrently, or the second recording channel may be used for simultaneous DTA-EGA with the appropriate sample holder assembly, a hot-wire gas thermal conductivity cell and a power supply assembly. The power supply is also available in combination with a recorder to complete the operational

(*Continued on page A112*)

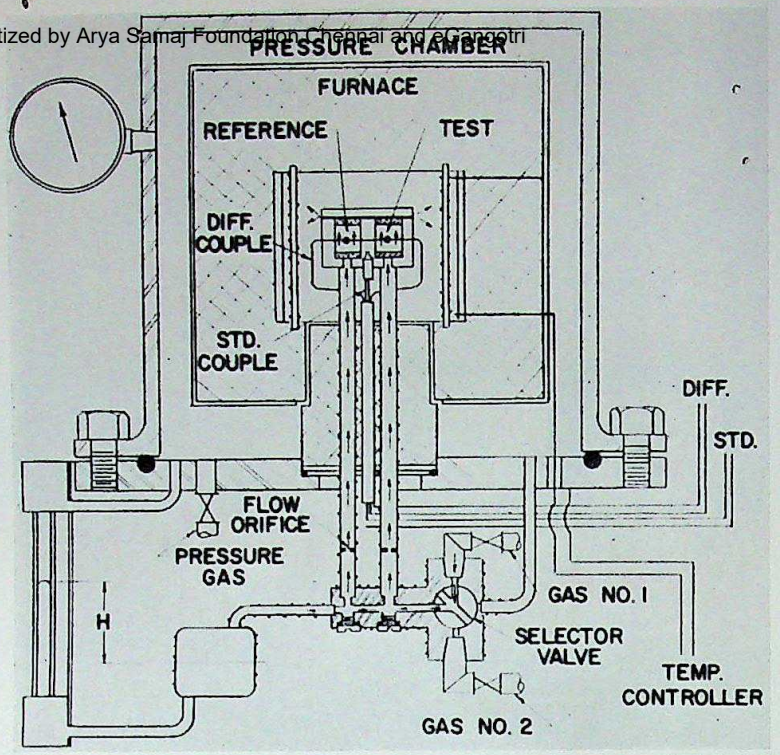


Figure 11. Schematic drawing of the pressure chamber and furnace platform assembly in the R. L. Stone DTA apparatus.

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The nucleic bases, nucleotides and related structures are also depicted in detail. The purines and pyrimidines are shown in both keto and enol forms. Instructions for hydrogen bonding of base pairs are given.

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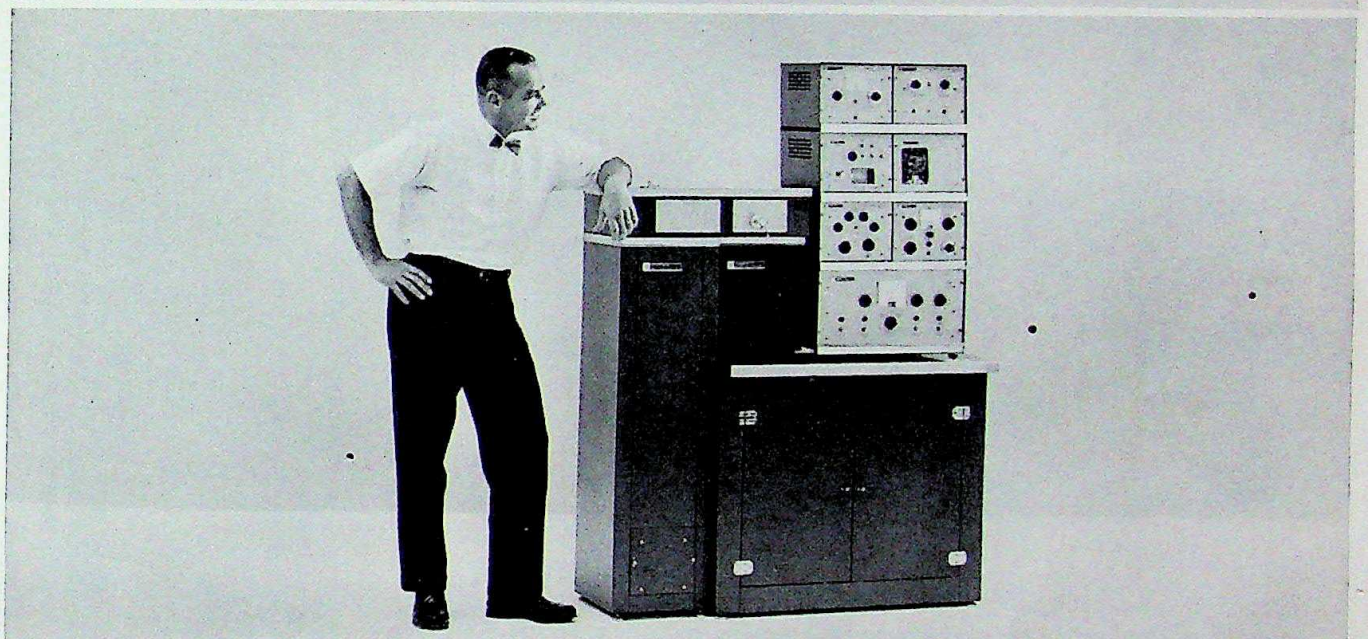
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assembly shown in Figure 12. A new thermobalance is available for thermogravimetric evaluations that may be used with either a separate control system or the DTA recorder-controller assembly.

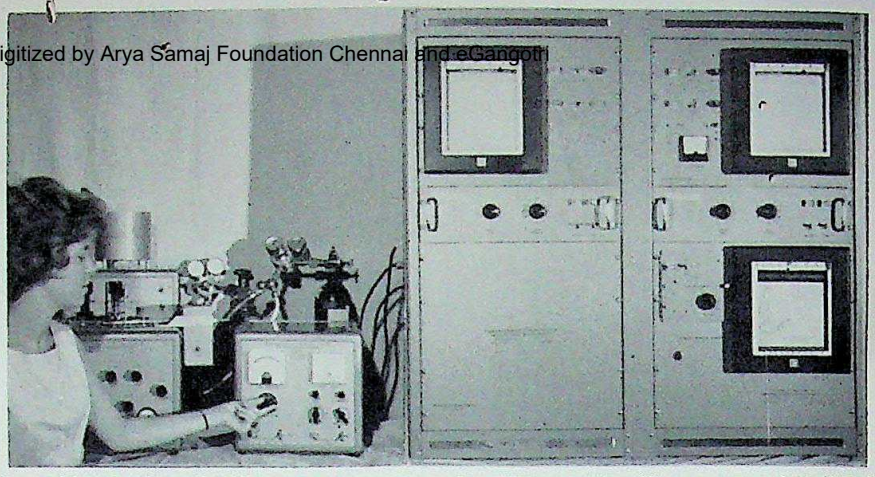


Figure 12. R. L. Stone Co. DTA apparatus consisting of the DTA assembly, effluence gas analysis (EGA) detector and power supply, and recorder-programmer assembly.

Technical Equipment Corp.

The Deltatherm ($5875), manufactured by Technical Equipment Corp. in Denver, Colorado, is a console mounted DTA apparatus, Figure 13. This instrument incorporates a temperature programing system and four-channel dry stylus electrosensitive paper recorder, with twin furnace positions and interchangeable multi-sample plug-in blocks having gold plated thermocouple connecting plugs and printed circuits for the interconnecting thermocouples, Figure 14. A series of metal and ceramic blocks are available for pressure, vacuum, and dynamic gas atmosphere studies with nine wells to accommodate four sample-inert reference pairs and one for the control thermocouple. The basic unit is equipped for a fixed heating rate of 10°C per minute but may be replaced with an optional rate-control unit for more closely controlled heating rates of 2 to 20°C per minute that are obtained with interchangeable

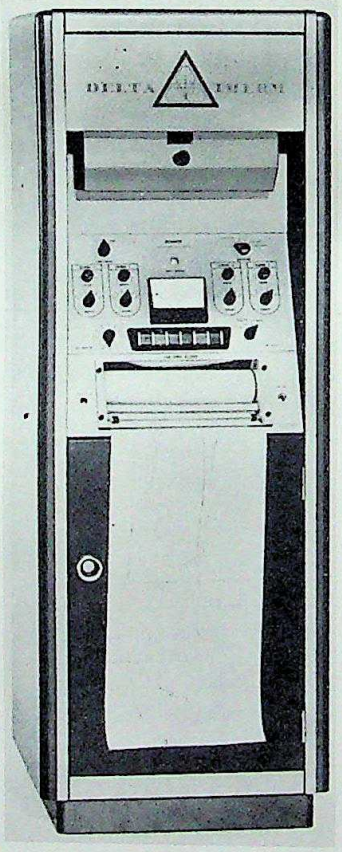
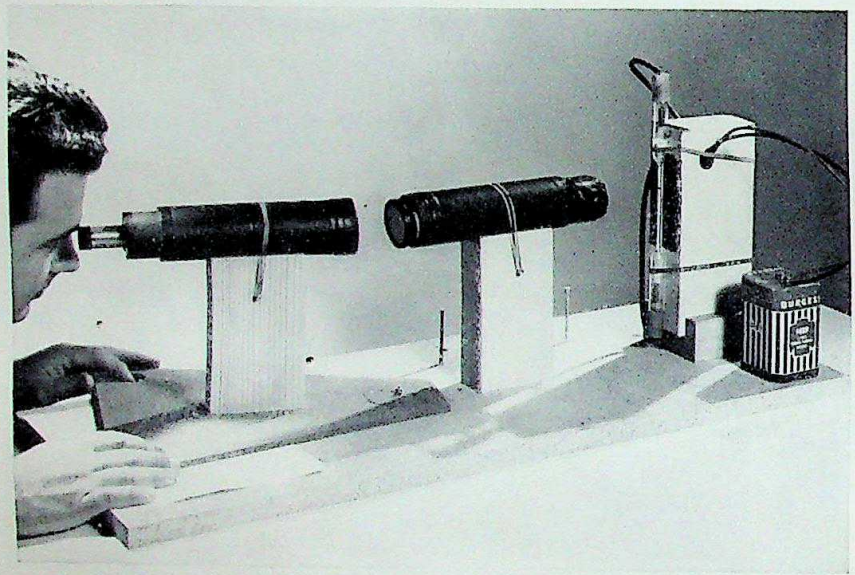


Figure 13. Technical Equipment Corp. Deltatherm.

gears. A group of six plug-in stable dc amplifiers with printed circuitry and transistorized solid state choppers are used for the four sample-reference differential temperature channels, the temperature indicator that also provides a series of solid calibration lines across the chart

(Continued on page A114)

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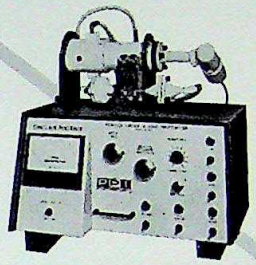
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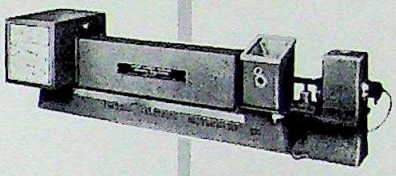
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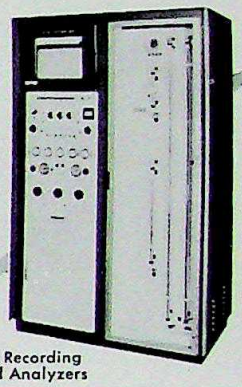
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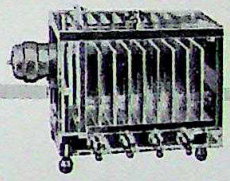


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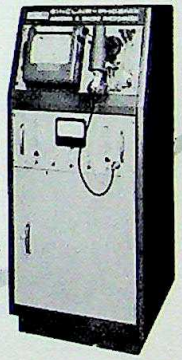


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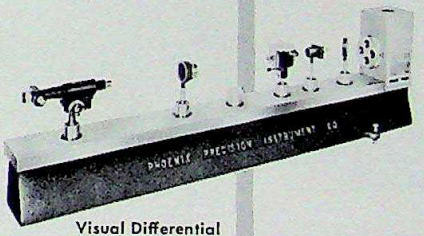
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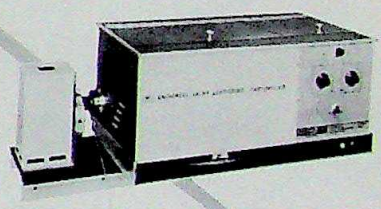
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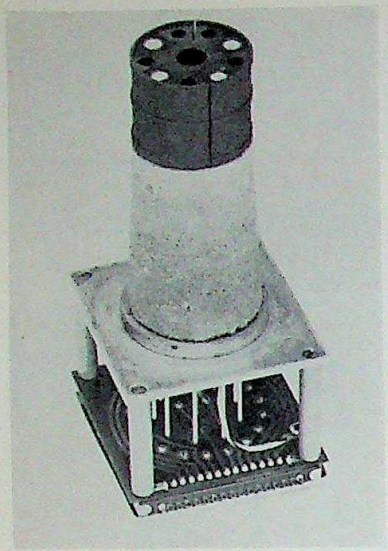


Figure 14. Multiple sample holder with printed circuitry and plug-in module construction used in Deltatherm.

at 50°C intervals, and in the rate control temperature programer, Figure 15. The sensitivity of 25 μv per inch (0.6°C/in.) may be used over the full 12 in. width of the recorder with overlap of all four traces. Any of four fixed levels of step attenuation may be chosen to minimize or eliminate this overlap. The reference well temperature is constantly displayed for visual panel monitoring on a printed tape potentiometer. Provided for selector-switch read-out of line voltage, furnace current, or recorder chart position for each of the four DTA traces. The use of two furnaces, and an optional third furnace that can be operated externally to the apparatus, allows for virtually continuous operation of the instrument. A companion thermobalance has been developed for complementary thermogravimetric studies.

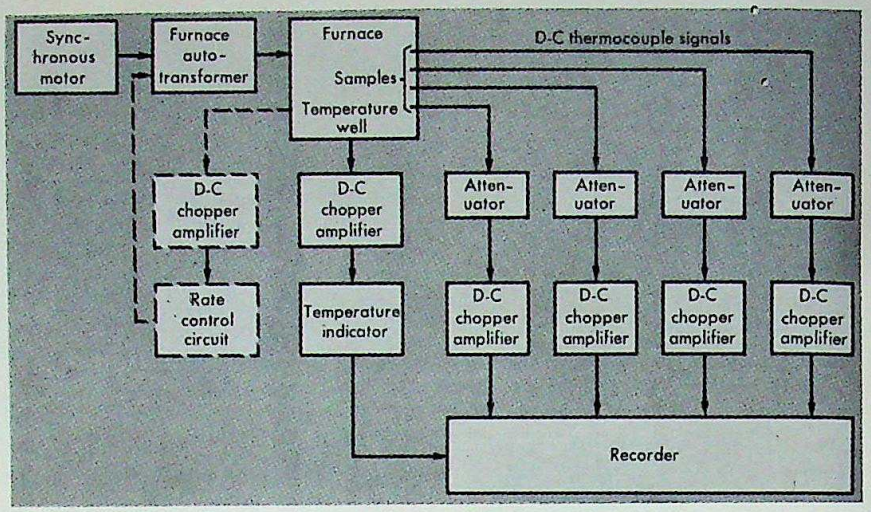


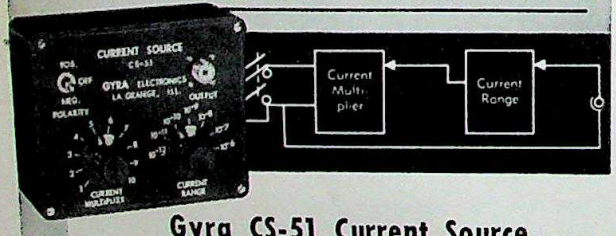
Figure 15. Block diagram showing operation of the Deltatherm DTA apparatus.

Summary

Although the major contributions involving DTA studies have been made by investigators who have constructed or assembled their own apparatus, many of which are described in the following references, it is obvious that they did so because well designed instrument packages were not commercially available. This situation has now been greatly alleviated by several companies, as previously described. Nevertheless, those with limited equipment budgets should find many useful suggestions for instrumentation and experiments in the references cited below. This survey of DTA instruments has been restricted to instruments that are domestically manufactured

(*Continued on page A116*)

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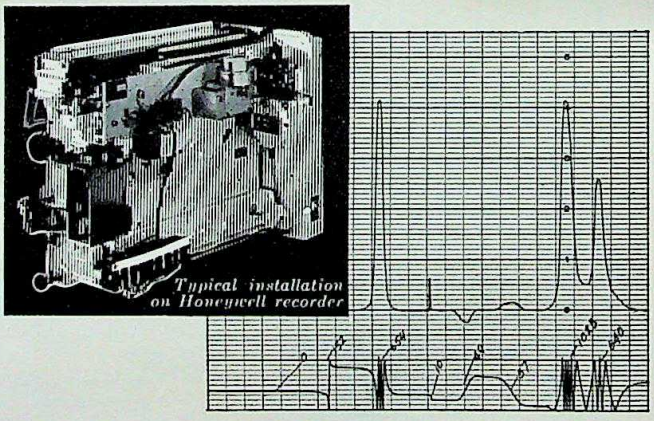
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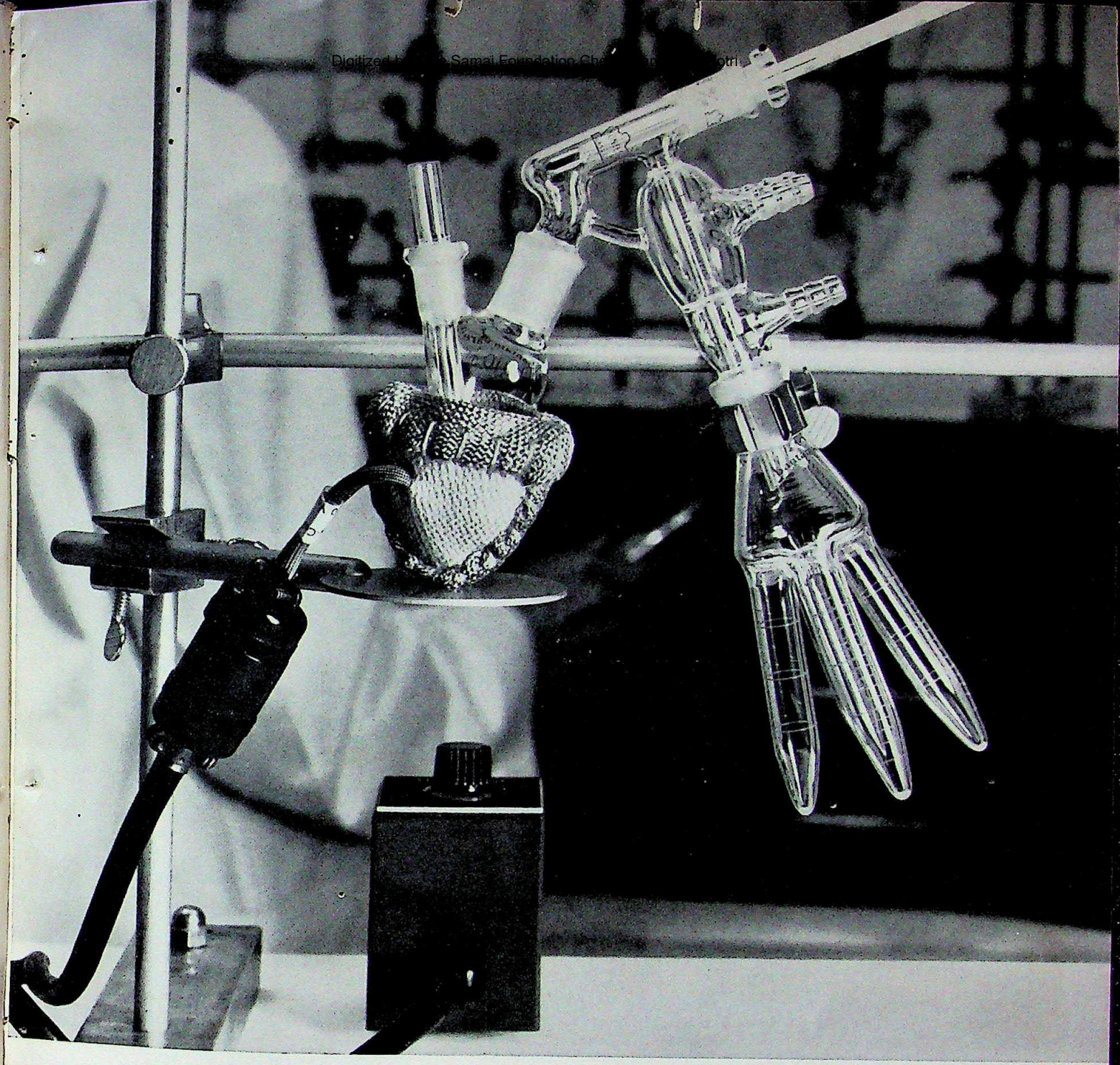
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because their foreign counterparts are not readily available at this time.

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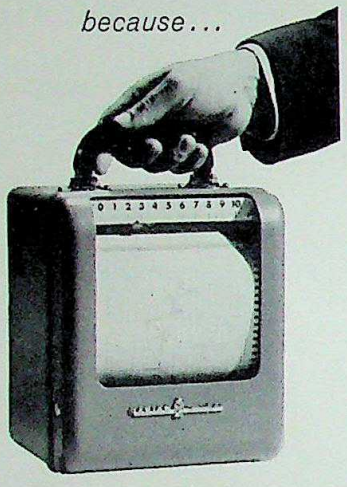
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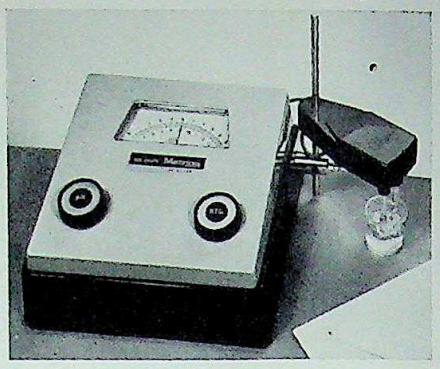
Nine full-scale voltage ranges from 10 mv to 100 v d. c. are switch-selected on the B-1 input chassis, adapting the Varian G-11A to almost any recording need. Other chassis let you use the G-11A for temperature recording from −200° C to +1500° C or 1 mA current recording. The G-11A is portable—goes anywhere. And it's compact—never in the way.

1% accuracy; 1 second full-scale balance; chart speeds from 1/8"/hour to 60"/minute; rack mounting available. A wide range of options and accessories. Prices start at $515. Complete details and specifications from Recorder Products.

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COLEMAN



Metrion® pH Meter

...premium performance without price penalty

The Coleman Metrion® pH Meter offers you performance levels usually available only with laboratory pH meters priced in the $300-and-up range.

ACCURACY—to ±0.05 pH with reproducibility of ±0.02 pH.

VERSATILITY—covers the full 0-14 pH range on overlapping duplex scales.

ELECTRODES—uses any of the full line of Coleman electrodes; adapts to electrodes of other manufacture.

TEMPERATURE CORRECTION—calibration control simultaneously provides accurate correction for temperature effect.

SAMPLE SIZE—requires only 4 ml of sample using Coleman screwbase electrodes.

STABILITY—fully stabilized against line voltage changes from 95 to 125 volts.

PRICE—only $139.00

Ask for Bulletin BB-257, and a demonstration.

COLEMAN

COLEMAN INSTRUMENTS, INC.

MAYWOOD, ILLINOIS

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COLEMAN

Coleman instrumentation for automated combustion analysis

Complete determinations in only 8 minutes
. . . improve accuracy and reproducibility
. . . eliminate errors due to variations in analytical technique.

For nitrogen analysis—the time proven Coleman Nitrogen Analyzer is unequalled in speed, reproducibility and convenience by any traditional method for total nitrogen determination. It provides rapid and automatic performance of all steps required in the analysis.

WIDE APPLICATION—the instrument is ideal for virtually any solid or liquid material that dissociates at temperatures up to 1100° C.—including materials usually analyzed by time-consuming Kjeldahl procedures.

DIRECT READING—results of the analysis are displayed on a digital counter.

VOLUME OUTPUT—8-minute instrument operating cycle permits a single operator to perform up to 40 analyses per day. There is no need to wait several hours for results needed right away.

FULL AUTOMATION—from sample input to final readout, all procedure variables are carried out automatically. Titrations are not necessary.

HIGH ACCURACY—the instrument determines nitrogen in substances containing as little as 0.01% nitrogen to more than 75%. At the 10% level, it achieves an accuracy of better than ±0.15%.

Write for descriptive literature and reprint of complete evaluation report by Southern Research Institute.



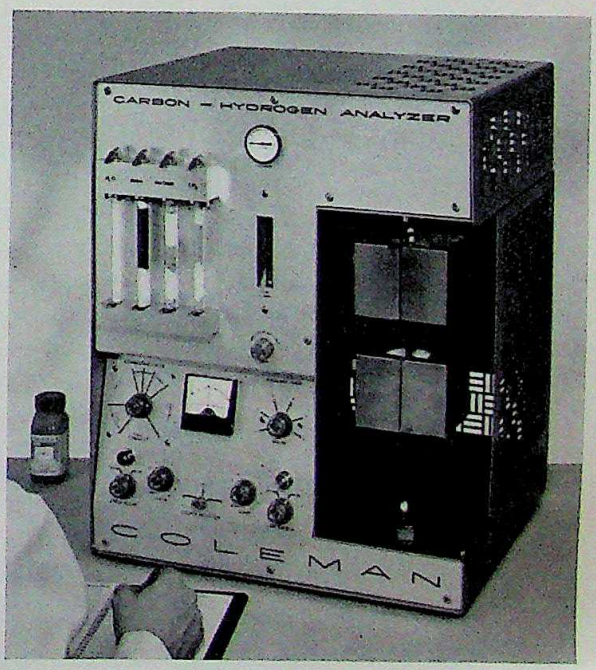
For carbon and hydrogen analysis—the Coleman Carbon-Hydrogen Analyzer, an automated combustion train, offers substantial advantages over conventional methods. Greater speed, convenience and improvements in precision and accuracy result from the instrument's performing all operations in exactly the same manner. Benefits include:

VERSATILITY—Variables of the combustion cycle are readily programmed to meet requirements of a wide variety of sample materials—hydrocarbons as well as materials containing oxygen, nitrogen, sulfur and halogens. Specially-prepared silver vanadate and manganese dioxide reagents, available from Coleman, permit analysis of difficult samples.

RANGE—the instrument is valuable in laboratories concerned with feeds, pharmaceuticals, petroleum, organic intermediates, heavy chemicals and biological materials. It is used for analysis of materials containing 10-98% carbon and 0.5-15% hydrogen.

ACCURACY—automatic control of the major variables in the analysis—temperatures, flow rates, combustion periods—provides high analytical accuracy. For routine work, the instrument results correspond to theory ±0.2% carbon and ±0.2% hydrogen.

Ask for Bulletin BB-275.



COLEMAN INSTRUMENTS, INC., MAYWOOD, ILLINOIS

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new techniques for . . .

THIN-LAYER CHROMATOGRAPHY

Have you investigated the advantages of thin-layer chromatography? In addition to the normal ascending thin-layer chromatography, equipment is now available for all of the following new procedures:

1. PREPARATIVE TLC
2. CONTINUOUS FLOW TLC
3. TWO-DIMENSIONAL TLC
4. HORIZONTAL TLC
5. DESCENDING TLC
6. SATURATED ATMOSPHERE TLC
7. TEMPERATURE CONTROLLED TLC
8. APPLICATION CHAMBER FOR CONTROLLED ATMOSPHERES WITH SENSITIVE MATERIALS
9. DEVELOPING CHAMBER FOR CONTROLLED ATMOSPHERES



The DESAGA/BRINKMANN Apparatus for TLC, including the standard and adjustable applicators, is the most widely used in this field. In addition to the above new techniques—new standard accessories and new adsorbents are also available. About $250 is required for the basic equipment.

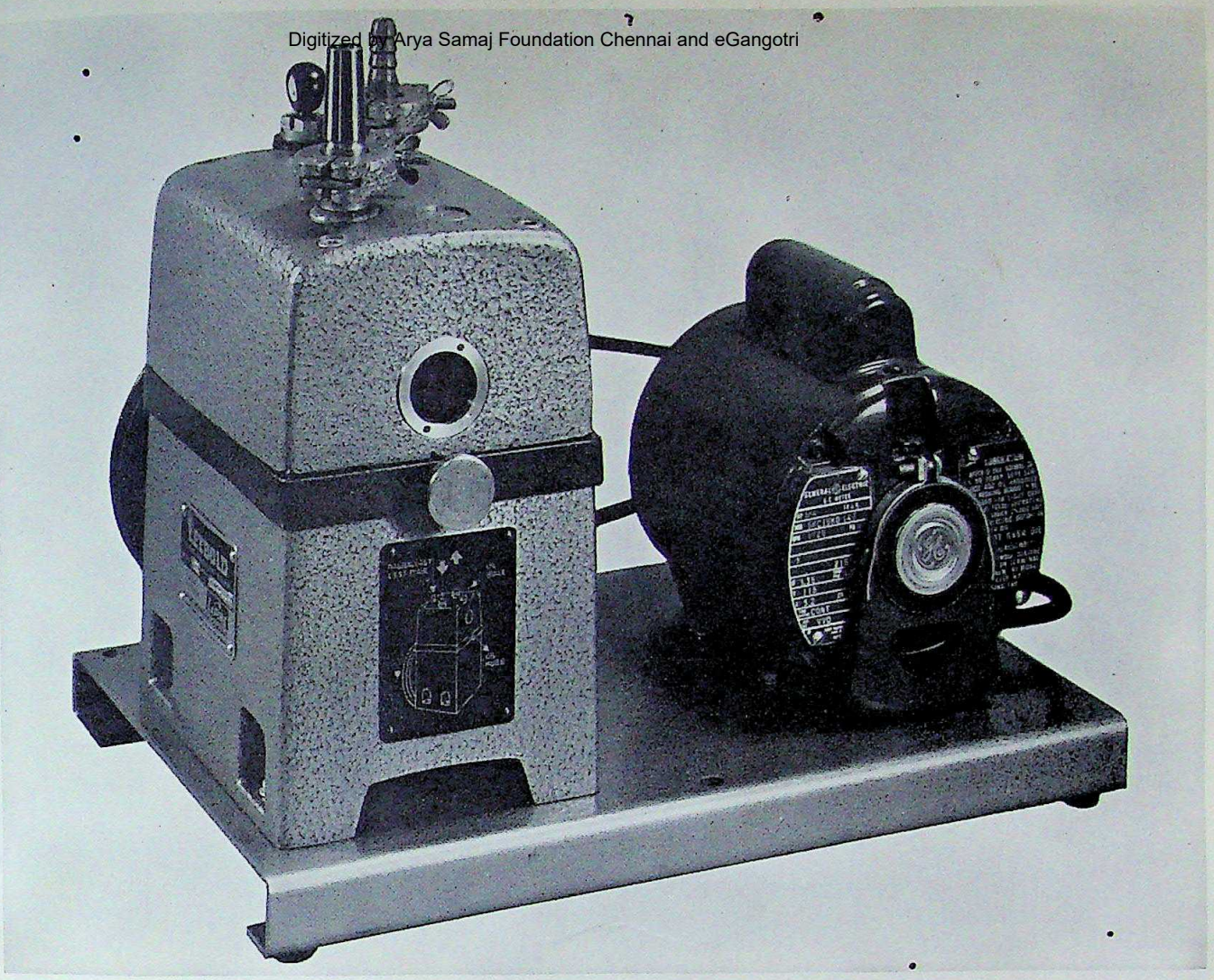
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BRINKMANN INSTRUMENTS, INC., 115 CUTTER MILL ROAD, GREAT NECK, N.Y.

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VACUUM MASTER

. . . an apt name for the handsome new series of Leybold high vacuum pumps. And they perform handsomely, too! The model 2 D (illustrated) and three companion high vacuum pumps further the Leybold tradition of fine performance and reliability. Some of their excellent features: Low ultimate pressure . . . Low noise level . . . High water vapor tolerance . . . Gas ballast operation at the twist of a knob . . . Visibile oil level . . . Large oil reservoir . . . No oil foaming . . . Connections in seconds with Small Flange Fittings. Brief specifications are given below. Write for a complete bulletin on pumps and fittings.

CAT. NO.	MODEL	FREE AIR DISPLACEMENT Liters/Minute	ULTIMATE VACUUM, MM HG w/o Gas Ballast	w/Gas Ballast	PRICE
352-71	2 S	43.3	$<2\times10^{-2}$	<1	$170.00
351-74	2 D	43.3	$<2\times10^{-4}$	1×10^{-2}	255.00
352-76	6 S	107.0	$<2\times10^{-2}$	<1	265.00
352-78	6 D	107.0	$<2\times10^{-4}$	1×10^{-2}	345.00

Delivery from stock on all models.

LAPINE

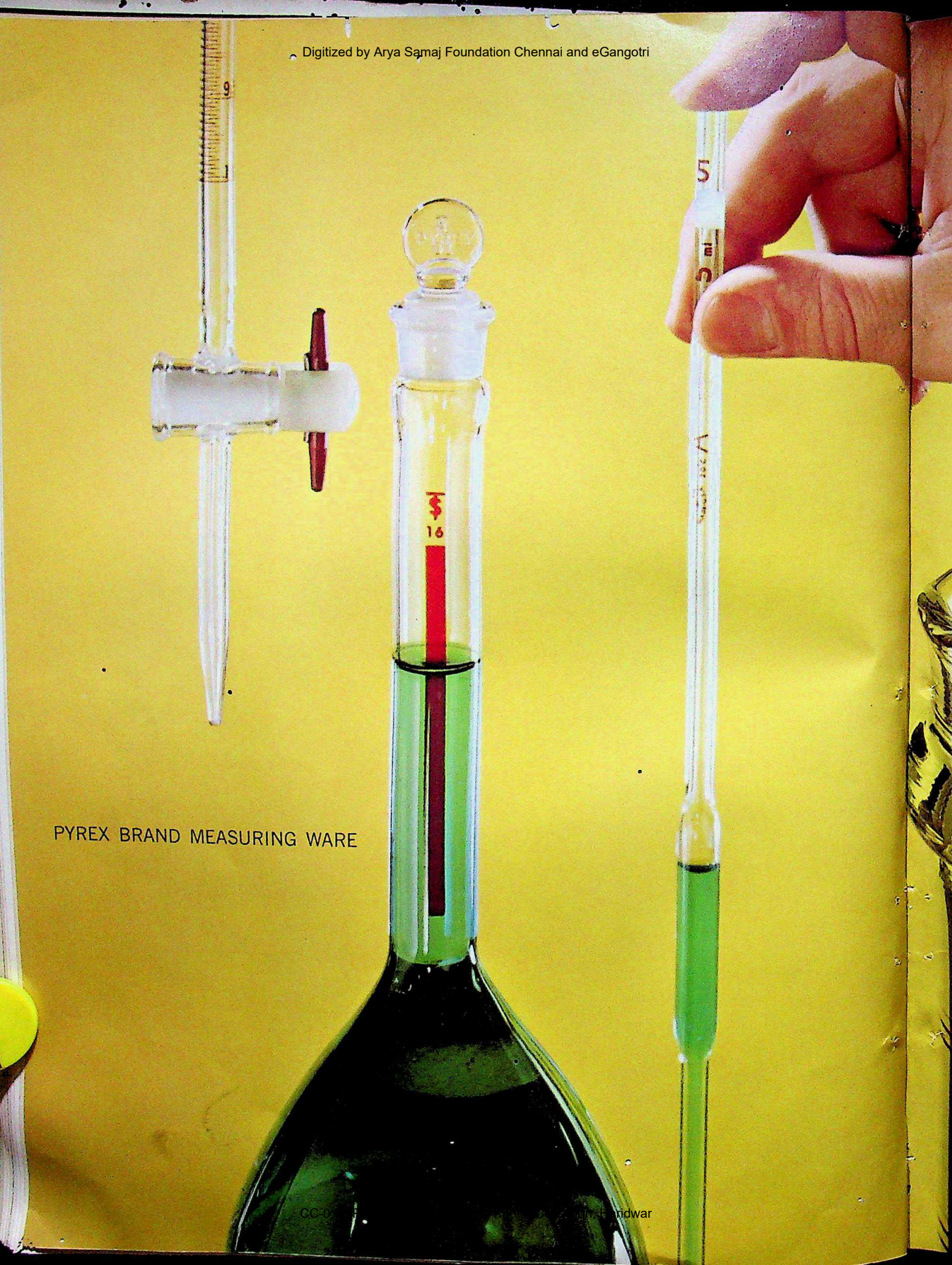
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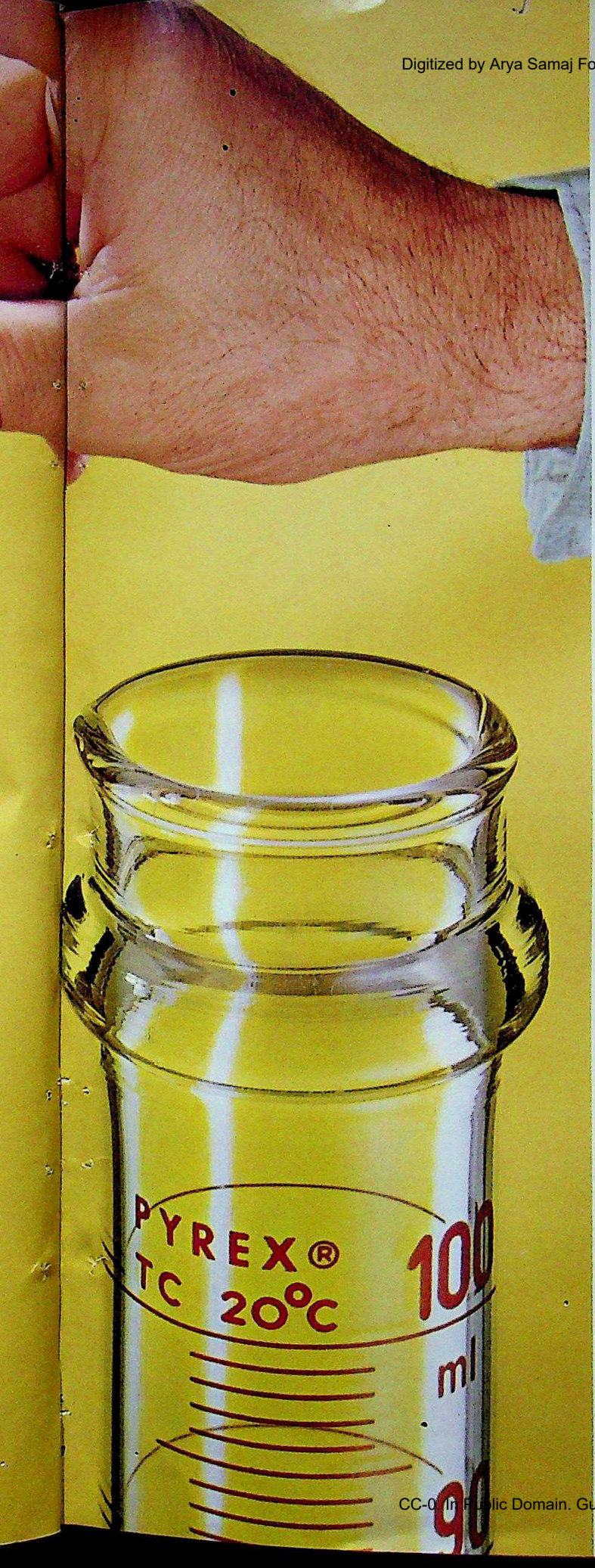
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Does measuring ware have to be delicate to be accurate?

Not when you've put more than 40 years into the making of PYREX® measuring ware that's tough as well as precise.

You *know* PYREX ware is accurate. It must be to pass the tough tolerance tests we put it through. But, even more important, you learn that you *use* this accuracy longer, simply because the ware *lasts* longer.

We start with the best-balanced borosilicate glass ever made. It's proportioned in flask walls to give strength to what could be a fragile bubble. Then we teach machines to reproduce that proportion a million times without a variable.

We've added other machines that draw tubing so accurately you can cut a uniformly perfect pipet or buret from any foot in a mile of it.

We've put in other innovations—such as ACCU-RED™ graduations, which are fused into the glass surface without an etch pattern to weaken it, and the extra bevel that strengthens our pipet and buret tips.

These are the factors which add up to the *big plus*—accuracy plus long life. They are the reasons why PYREX labware catalog LG-2 is your best source of accuracy *plus* strength . . . by the piece, the case, or the carload. Discounts run as high as 28%. Laboratory Glassware Dept., 7105 Crystal Street, Corning Glass Works, Corning, N. Y.

RUB THE TIP OF A PYREX PIPET. It's as round and smooth as a ball-point pen, to reduce snagging and chipping. We put two bevels on every tip to do that job. Accurate-bore tubing gives you uniform accuracy and strength from tip to top.

LOOK WHERE THE STOPCOCK JOINS THE BODY OF A PYREX BURET. We add glass to add strength there and in the shell of the stopcock itself. Double-beveled tips. Accurate-bore tubing. For real ease of operation, try our unique reverse-taper Teflon* plug stopcock† model.

FEEL THE TOP OF A PYREX CYLINDER. We put extra glass around it and fire polish. On some models, we add a husky shoulder of glass to cushion against falls—it can't ride up and down, come off, or get lost. To make falls less likely and to reduce breakage if one should fall, we *weld* flatly pressed, hexagonal bases onto our cylinders.

TRY PYREX VOLUMETRIC FLASKS. Use them for six months and match them against *any* other. See if they don't give you longer life as well as accuracy. Heavy-neck tubing, skillfully sealed to machine-proportioned bodies, give you rugged units of strength.

*Du Pont trademark
†Licensed under U.S. Patent 2,876,985

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TYPE H-5

MODERN INSTRUMENTS ENCOURAGE INTEREST IN SCIENCE

Hundreds of colleges and universities have adopted Mettler H Analytical balances for classroom use because of the belief that modern science should be taught with modern instruments.

Now, a new series of Mettler balances specifically fits the performance requirements of secondary schools.

Mettler H Multi-purpose balances provide, at reasonable cost, completely modern instruments capable of rapid weighings to precisions previously unattainable on conventional high school balances.

Students weigh on instruments with an optical scale range of 1 gram in 10 mg scale divisions while developing familiarity with optical micrometers or verniers.

TYPE	CAPACITY	OPTICAL RANGE	PRECISION	PRICE
H-5	160 g	1200 mg	±0.1 mg	650.00
H-4	160 g	1200 mg	±0.3 mg	585.00
H-3	160 g	1200 mg	±0.5 mg	550.00

PRECISION is given as the standard deviation of repeated weighings of one and the same quantity.

For more information about H Multi-purpose balances write:

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Out of the EDITOR'S BASKET

Edited by William G. Kessel

When writing for additional information about new products or for new literature, your inquiry will receive prompt attention if you write on your firm or Institution letterhead and mention the Journal of Chemical Education and the date of the particular issue. Pamphlets, booklets and similar literature are gratis unless otherwise specified.

New Apparatus and Equipment

▶ A closed system, magnetically-actuated, fraction collector is being manufactured by Kontes Glass Co., Vineland, New Jersey. Without interrupting or disturbing a vacuum distillation in any way, the device provides for separation and collection of six 15 ml fractions or four 50 ml fractions, depending upon tubes and tube holders used. Ask for *Bulletin 1062.*

▶ Speeds to 25,000 Rpm. and forces up to 80,000 × G are features of a new, refrigerated, ultra-superspeed vacuum centrifuge "Vac-Fuge," Model 25 introduced by Lourdes Instrument Corp., 656-78 Montauk Ave., Brooklyn 8, N. Y.

▶ Radiation Instrument Development Laboratory, Inc., 4501 W. North Ave., Melrose Park, Illinois, offers a new precision Nanosecond pulse generator which is now available from stock. Rise and fall time of less than 0.5 nanosecond. Pulse widths of 0.5 to over 1000 nanoseconds with 4 internally calibrated pulse widths provided.

▶ Gas content of ultra-micro samples can be more easily determined with the new Motorized Natelson Microgasometer. Self-contained, this greatly improved instrument is available from Scientific Industries, 220-05 97th Ave., Queens Village 29, New York.

▶ A steady state distribution machine that can be programmed to produce continuously a gram an hour of high purity materials from complex mixtures has been introduced by Corning Glass Works, Corning, New York. The instrument is especially useful to scientists involved with research into anti-biotic separations, biochemistry, essential oils and fusion materials and natural products.

▶ The marketing of a new line of laboratory oxygen measuring equipment has been announced by the Scientific and Process Instruments Division of Beckman Instruments, Inc., 2500 Harbor Blvd., Fullerton, California. The new device, Model 777, is suitable for the determination of oxygen in gases or of dissolved oxygen in aqueous or non-aqueous solutions.

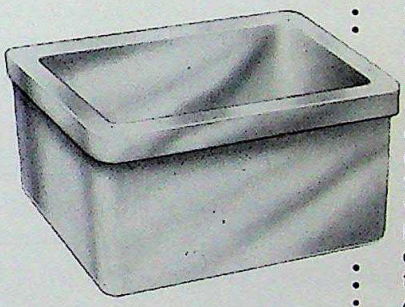
▶ Laboratory analyses in series of solutions or extracts often are slowed up considerably because of the time required to measure and accurately weigh miniscule doses of liquids without spilling them. Now, however, an electronic dispensing apparatus made by a leading chemical instrument firm in Holland, Reyers and Zoon, improves on conventional methods For additional details, readers may write to the Netherlands Consulate General Commercial Division, 10 Rockefeller Plaza, New York 20, N. Y.

▶ New from the Voland Corp., 27 Centre Ave., New Rochelle, New York, is a significant forward step in the design of precision analytical balances. The new unit, Model Pointer 160-A, is a direct-reading single-pan balance with a capacity of 160 grams which is readable instantly and exactly to 0.1 mg.

▶ Numec Instruments and Controls Corp., Apollo, Pennsylvania, announces the availability of a new analytical instrument, the Numec Electronic Controlled Potential Coulometric Titrator. Based on the ORNL Model Q2005 X50 titrator, this instrument provides rapid analysis of small quantities of materials with an accuracy and precision as good as or better than usually obtained with larger

(*Continued on page A124*)

"U. S." CHEMICAL PORCELAIN LAB SINKS



THE LAB SINKS WITH THE *Lifetime Guarantee*

The laboratory sinks which we manufacture from chemical porcelain are completely impervious and corrosion-proof. Their resistance to all corrosive agents (except hydrofluoric acid) is not limited to the glazed surfaces. Both the glaze, and the sink body itself, are made of the same basic corrosion-proof materials. Thus, there is practically no difference between the corrosion resistance of the glaze and that of the sink body.

We, therefore, make the following guarantee:

We guarantee, for the life of the building in which it is installed, that this sink will not be destroyed by the action of corrosive agents, regardless of whether glazed or unglazed surfaces are exposed to corrosion.

We also guarantee that this sink will not be damaged or destroyed by temperature changes or mechanical stresses encountered in normal laboratory usage.

(This guarantee does not include mechanical damage due to gross carelessness during installation or due to heavy impact, nor does it include etching of the sink surface by hydrofluoric acid. Natural and artificial silicates are attacked by hydrofluoric acid, and if such acid is emptied into sinks, the sinks should be flushed with water immediately to prevent damage to the glaze.)

Under the terms of this guarantee we will furnish without charge, freight prepaid, a new sink for any sink which fails to meet the service warranty above. This guarantee does not include any installation costs. We reserve the right to request the return of the defective sink, freight collect.

For complete details contact your Laboratory Furniture Manufacturer or write direct for free Bulletin L-10.

Chemical Ceramics Division

U. S. STONEWARE
AKRON 9, OHIO

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A *NEW* CONCEPT TO IMPROVE LABORATORY TOP SURFACING . . .



GREGG LABORATORY TOP installation at Metabolic Research Laboratory, Lahey Clinic, Boston, Mass.

GREGG

LABORATORY TOPS

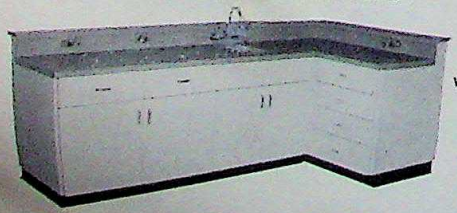
with *CHEM-GUARD

***(manufactured by CONOLITE)**

Chem-Guard, is a non-porous surface material designed to withstand all conditions normally present in research, commercial or educational laboratories. Its deep wearing surface, which extends in even density, through to the reinforcing material, is free of fibers and its gray tone offers a non-glare working area. A heavy resin overlay insures a long useable life.

Only minimum maintenance is needed for Chem-Guard, because surface scratches can be easily sanded with emery cloth or buffed with steel wool. Severe damage is easily repaired with a color-matched, caulking compound. After sanding, buffing or caulking, the refreshed surface maintains the identical high resistance to chemicals as the original surface.

- GREGG TOPS are seamless and fully formed in sections up to ten feet in length. Longer lengths are manufactured with factory fitted "lock joints" and sealed with chemical resistant caulking.
- GREGG TOPS are light in weight for easier handling, permitting longer length installations with minimum labor costs.
- GREGG TOPS are easily fabricated at the job-site, with standard woodworking tools, to provide for last minute changes or additional laboratory services.
- GREGG TOPS are soft and warm to the touch. They dull the noise normally created when glassware or instruments are dropped on the surface.
- GREGG TOPS are particularly suited for laboratories working with radio-active chemicals because of their extremely low absorption factor and their fully formed seamless surfaces which eliminate areas for build up or contamination.
- GREGG TOPS *do not have an applied or polished surface* which loses resistance value when scratched or worn.



For more information write for brochure #850 and test reports

GREGG LABORATORY TOPS

NASHUA, NEW HAMPSHIRE

quantities using conventional potentiometric analysis.

▶ Penn-Chem Corp. of 238 North Marshall Street, Lancaster, Pennsylvania, introduces a new line of protective wire racks for the safe storage of condensers, burettes, pipettes, thermometers, distillation columns and various other glassware items of similar shape, usually loosely stored in drawers in the chemical laboratory.

▶ The Loenco thermal conductivity Transducer is a highly sensitive, bridge-balance operated detector for measuring thermal conductivity or gas flow at temperatures up to 500°C. For additional information contact Loenco, Inc., 2092 No. Lincoln Ave., Altadena, California.

▶ Bausch & Lomb, Inc. has just introduced its first completely electronic instrument—the VOM-5 Strip Chart Recorder. The instrument's leading feature is an ability to record multiple inputs directly: for example, resistance, milliamps, or dc volts, without the use of external converters. For complete information, write to Bausch & Lomb, Inc., Rochester 2, New York, specifying *Catalogue D-2032*.

▶ A new pump to transfer liquids, slurries or solids in solution has been introduced by Sigmamotor Inc., 24 No. Main St., Middleport, New York. Called the Vibro-Pump, the new design has no rotating shaft, bearings or stuffing boxes yet operates on the centrifugal principle.

▶ Complete information on the CRS-1 chromatograph digital integrator may be obtained from Infotronics Corp., 1401 So. Post Oak Rd., Houston 27, Texas.

▶ Pacific Transducer Corp. of 11836 W. Pico Blvd., Los Angeles 64, California announces the development of a new approach to measuring surface temperatures from 0 to 1000°F. The instrument utilizes a tempered glass dial. The bimetal coil as well as the surface being measured is visible through the dial.

▶ A new micro melting point apparatus announced recently by the National Instrument Co., 4119 Fordleigh Rd., Baltimore 15, Maryland, provides a simple, accurate means for determining the melting points of single crystals, micro or macro particles. Determinations may be made up to 360°C with an accuracy of ±0.5°C.

New Apparatus and Equipment

▶ An easy-to-use first aid instrument, the G-S Eye Sweep is available from General Scientific Equipment Co., Limekiln Pike and Williams Ave., Philadelphia 50, Pennsylvania. The G-S Eye Sweep is a double purpose magnet-and-loop which re-

(*Continued on page A125*)

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Out of the EDITOR'S BASKET

moves metallic and non-magnetic particles, dirt, chips and other foreign matter from the eye. Sterilization does not affect the magnetic properties of the loop. The G-S Eye Sweep is packaged in a hard rubber carrying case. Write General Scientific for complete information.

New Literature

● Industrial Components, 4167 Canyon Rd., Beaverton, Oregon, is now making an improved version of the high-voltage square-wave generator described by Langdon Hedrick in the *Review of Scientific Instruments*. This generator is designed specifically to modulate the absorption cell of a microwave spectrograph although it has other applications. The generator will deliver 20 to 2000 volts of square wave into a 1000 pf load at 100 kc. The square wave is automatically zero-based and the amplitude is controlled by a single variable transformer.

Industrial Components can also furnish a complete 100 kc compatible receiving system including pre-amplifier, amplifier, detector and regulated power supply.

● Copies of the *Glossary of National Organic Chemicals* can be obtained by writing Dept. NA 131, National Aniline Div., 40 Rector St., New York 6, N. Y.

● A new 12 page product bulletin on the Model 720 dual column programmed temperature gas chromatograph has just been published by F & M Scientific Corp. of Route 41 and Starr Rd., Avondale, Pennsylvania.

● An eight-page, two-color catalogue describes and illustrates the comprehensive line of Esterline Angus Instrument Co., Inc. charts. Covered are curvilinear, rectilinear, inkless event recorder and ink type event recorder charts. For a copy write Esterline Angus Instrument Co., Inc., P. O. Box 596, Indianapolis 6, Indiana.

● Sargent *Bulletin SR-GC*, featuring the Model SR laboratory recorders for use in gas chromatography is now available from the manufacturer, E. H. Sargent & Co., 4647 W. Foster Ave., Dept. G. C., Chicago 30, Illinois.

● The new Varian Associates *Recorder Short Form Catalogue* pictures, describes, and gives basic technical and performance data on the complete line of Varian strip chart recorders. Write Varian Associates, 611 Hansen Way, Palo Alto, California, for a copy.

● For a free copy of *Atom Models to Construct Molecular Models of Organic Compounds*, write to LaPine Scientific Co., 6001 S. Knox Ave., Chicago 28, Illinois.

● The Bristol Co., Waterbury 20, Connecticut, offers a new 8-page *Oxygen*

(*Continued on page A126*)

The Improved Welch

CATHETOMETER

Significant recent engineering improvements in this instrument insure better performance than ever and more years of satisfactory service.

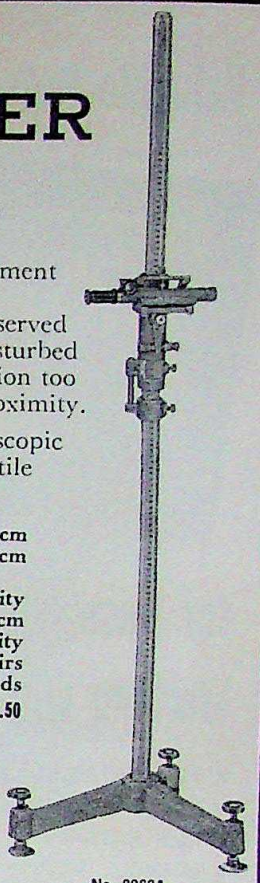
This cathetometer is designed for precise measurement of vertical distances through a range of 100 cm. It is particularly useful where the object to be observed is not conveniently accessible, or may easily be disturbed by physical contact, or must be located in a position too hazardous to permit the observer to be in close proximity.

It is also commonly employed for qualitative telescopic viewing within the laboratory because of its versatile positioning adjustments and over-all stability.

Vertical Range	100 cm
Smallest Reading by Vernier	0.05 cm
Telescope	
Working Distance	45 cm to Infinity
Angular Magnification	12X at 45 cm 8X at Infinity
Reticle	90-degree crosshairs
Level Sensitivity	50 Seconds

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Write for illustrated circular describing the many excellent features of this instrument



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A New Aid to Science and Teaching!

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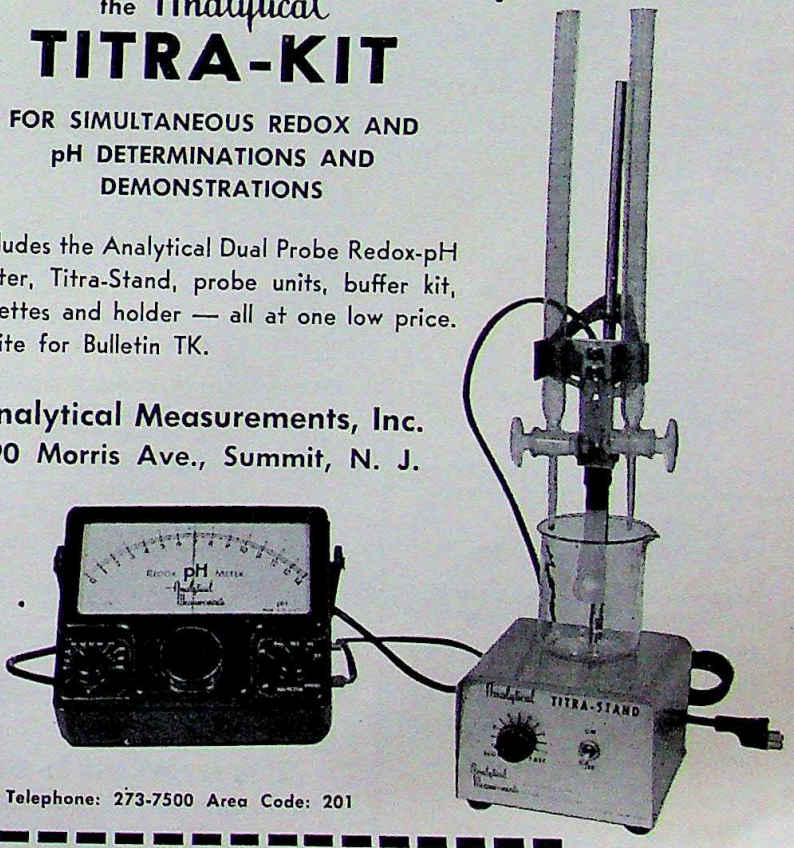
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FOR SIMULTANEOUS REDOX AND pH DETERMINATIONS AND DEMONSTRATIONS

Includes the Analytical Dual Probe Redox-pH Meter, Titra-Stand, probe units, buffer kit, burettes and holder — all at one low price. Write for Bulletin TK.

Analytical Measurements, Inc.

490 Morris Ave., Summit, N. J.

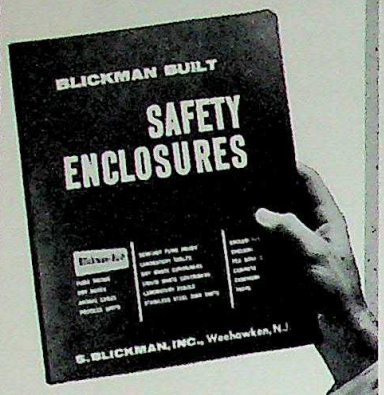


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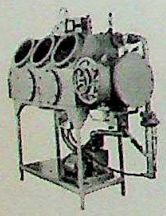
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This new book is a comprehensive reference on safety enclosures for handling a wide variety of hazardous substances. Profusely illustrated, it contains detailed descriptions of regular and vacuum dry boxes, biological safety cabinets, fume hoods, pressurized enclosures, controlled-atmosphere boxes, waste containers, laboratory furniture and sinks, process units and unitized dry box systems. You'll find an enclosure to meet almost any contamination or safety problem. Send for your copy now.



VACUUM DRY BOX
For controlled-atmosphere work. Stainless steel. One of many safety enclosures described.

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☐ Also send catalog on laboratory furniture

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COMPANY_____
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Blickman-Built for Years of Reliable Service

Out of the EDITOR'S BASKET

Analyzer Bulletin (W-1841). Using schematic drawings and photographic reproductions, the bulletin provides a useful text on oxygen analysis and oxygen content recording/controlling.

● Metal Hydrides Inc., 12-24 Congress St., Beverly, Massachusetts, has published a new technical bulletin #54, *Borohydrides In Polymerization Processes.* It describes recent work with borohydrides for purification of monomers; for stabilizing hydroxyl and carbonyl groups; and as a reducing component in redox polymerization systems.

● A revised 24 page booklet containing prices, specifications and ordering information for high purity rare gases, commercial gas mixtures and dispensing equipment is now available from Linde Co., Division of Union Carbide Corp., 270 Park Ave., New York 17, N. Y.

● Bel-Art Products of Pequannock, New Jersey, announces their new 1963 catalogue is now ready for distribution. Along with many new products, it features the most complete line of plastic laboratory ware for science and industry available from one source.

● A new 12-page brochure, *Bulletin 1004*, describing auto-gamma spectrometer systems for medical, biological and chemical research has just been published by Packard Instrument Co., Inc., Box 428, LaGrange, Illinois.

● Wilkens Instrument & Research of Walnut Creek, California, announces its first complete *Gas Chromatography Catalogue* just off the press. Together with its supplemental catalogue on accessories, supplies and materials, 34 pages are presented, showing the complete line of Aerograph instruments, and all other items needed for gas chromatography.

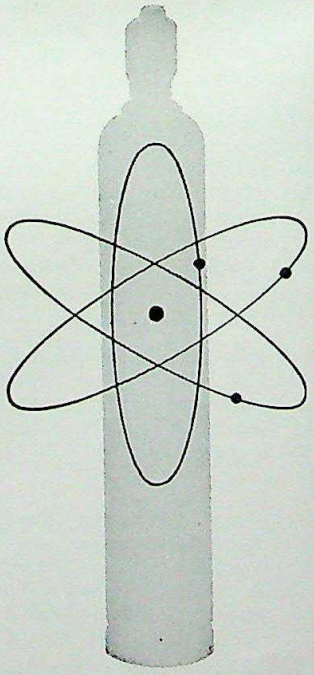
● A new 32 page *Mini-Lab Brochure* containing 27 new items is offered by Ace Glass Inc., Vineland, New Jersey. The Ace Mini-Lab line was introduced in 1950 and is, according to Ace Glass, the first especially designed and fully developed line of miniature glassware.

● Thorn Smith Laboratories, 1847 N. Main St., Royal Oak, Michigan, just published their 1963 catalogue giving over 1000 "unknowns" for chemistry student analysis.

● *Careers in Electronic Data Processing*, a booklet for guidance counselors and teachers is available from Hugh Allen, Director, Project on Information Processing, Box 201, Montclair State College, Upper Montclair, New Jersey.

● Their complete line of thermometers and hydrometers is now being shown in a new catalogue just released. *Catalogue*

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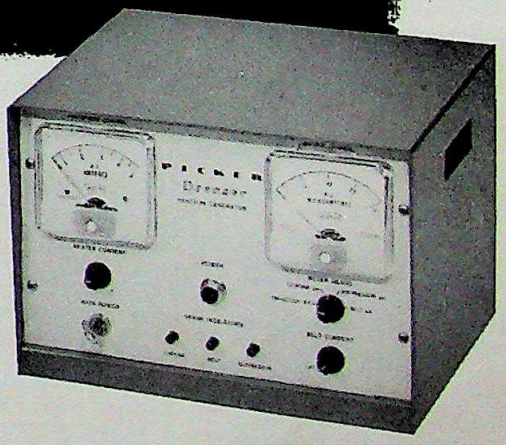
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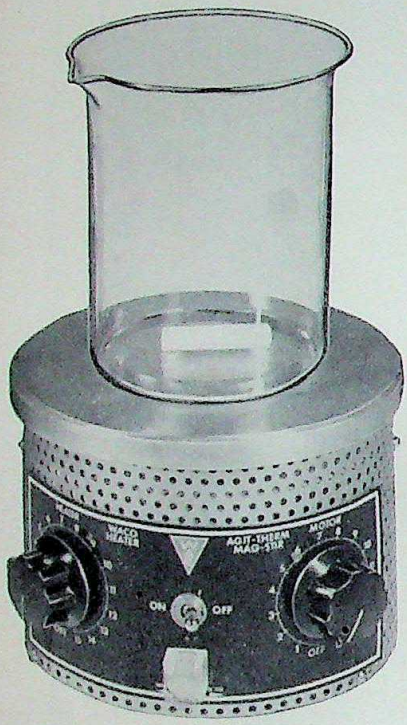
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628, a 30-page, multicolor booklet of the Brooklyn Thermometer Co. Inc., 217-11 Merrick Blvd., Springfield Gardens 13, New York, is available on request.

● A four-page, two-color catalogue sheet issued by Mikros, Inc., 7634 S. W. Capitol Highway, Portland 19, Oregon, describes the company's new electrostatic focusing EM-20 electron microscope, a completely self-contained instrument designed for functional operating simplicity and full time operation in the area of 35 angstrom units or better.

● An illustrated sixty-four page, two-color miniature catalogue *No. 600*, covering Blue M. Electric Company's complete line of electronic ovens, furnaces, magni-whirl baths, environmental cabinets and related temperature controlled equipment is available on request. Write Blue M. Electric Co., Blue Island, Illinois.

● For details on how to obtain a copy of the new Will *Catalogue 8*, contact any Will representative or subsidiary sales office, or write directly to: Will Scientific Inc., Box 1050, Rochester 3, New York.

● A compact, transistorized spectrophotometer-colorimeter which accepts both micro and conventional volumes is the subject of a new brochure *SB-205* from Spinco Division of Beckman Instruments, Inc., Palo Alto, California.

● Scientific Glass Apparatus Co. Inc., Bloomfield, New Jersey, has announced the publication of *Combined Catalogue 63*. According to the company, it consists of two separate volumes bound together for the convenience of the user, the 1136-page *General Section* and a 336-page *Inter-Joint Section*.

● A new 6-page brochure covering the operation and applications of the Disc Series 200 Chart Integrator has been released by Disc Instruments, Inc., 3014-B So. Halladay, Santa Ana, California.

● Precision recording, measuring and conversion instruments for laboratory and industrial use are described in a 16-page, 2-color catalogue available from the Houston Instrument Corp., 4950 Terminal Ave., Bellaire 101, Texas.

● Order the following by number from the OTS, U. S. Dept. of Commerce, Washington 25, D. C.:

60-51087 *Physical and Process Metallurgy and Physicochemical Research Methods*, No. 3, Proceedings of the Institute of Metallurgy, Academy of Sciences, USSR. edited by I. P. Bardin, published for the National Science Foundation. 1958. 336 pages. $3.50.

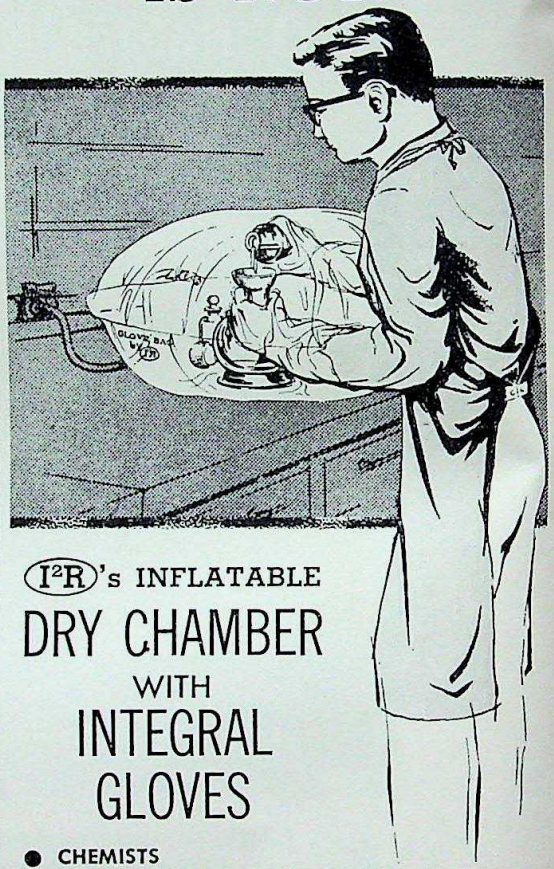
AD 272 855 *Study of Superoxidizers*. F. Martinez and others, Olin Mathieson Chemical Corp., for the U. S. Air Force. Dec. 1961. 63 pages. $1.75.

62-11021 *Detection and Analysis of Rare Elements*. A. P. Vinogradov and D. I. Ryabchikov, editors. Academy of Sciences of the USSR, Moscow. 1961. 744 pages. $7.50.

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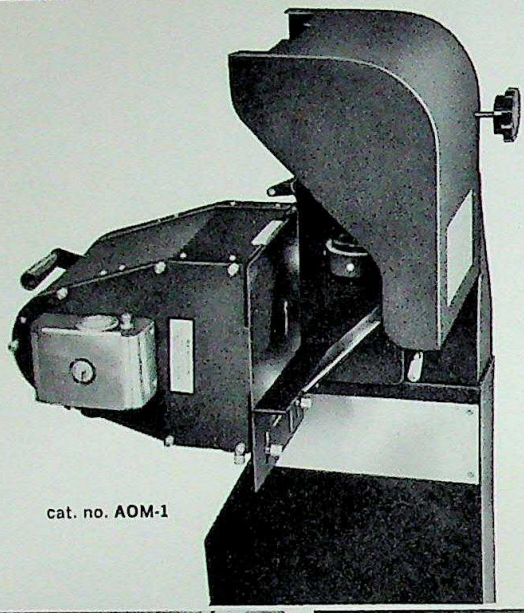
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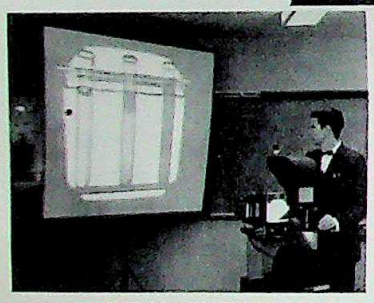
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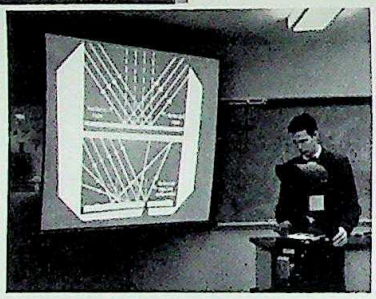
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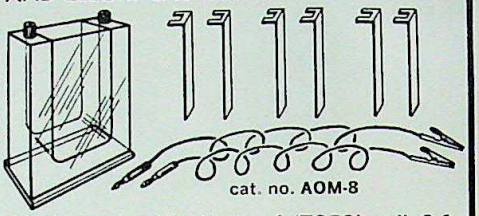
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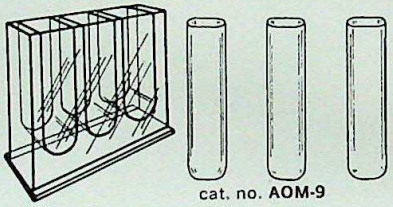
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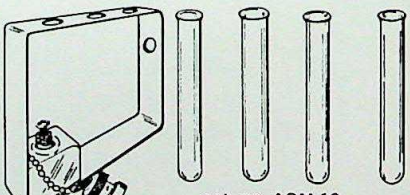
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2. OXYGEN

D. Some Oxidations *(continued)*

2. REACTIONS WITH AIR

Dem. 55—Iron Rusting in Air

To show: The rusting of iron in the air.

Materials: Steel wool, a square wide-mouth 2-oz bottle, a 4-in. length of 6 mm glass tubing, one-holed stopper for the bottle, a tall, thin drinking glass, HCl-aq.

Procedure: Stuff steel wool into the bottle. Wash once with the dilute HCl, then flush three times with water. Stopper, with the 6 mm tubing projecting outward. Invert in the drinking glass containing $^1/_2$-in. layer of water. Place on the projector.

Observations: The fresh surface of the steel wool rusts so rapidly that water rises in the 6 mm tubing several inches in 10 min. This is a dramatic experiment.

Note: Finely divided iron filings can also be used instead of steel wool.

Reference: MORRIS, S., AND HEADLEE, A. J. W., *J. Chem. Educ.*, **10**, 637 (1933).

Dem. 56—Heat of Rusting

To show: Heat of reaction from rusting iron.

Materials: Steel wool or iron filings, cell M°-1, dil. HCl or acetic acid.

Procedure: Wash steel wool in the square box of M°-1 first with dilute acetic or hydrochloric acid; then rinse three times with water to give a fresh iron surface. Wrap the steel wool around the bulb of the gas thermometer of cell M°-1, stuffing the steel wool into the plastic box. Put the rubber cap in place on M°-1.

Observations: The temperature in the box rises steadily as the steel wool begins to rust. In a few minutes the thermometer will have risen several degrees.

Reference: MORRIS, S., AND HEADLEE, A. J. W., **10**, 637 (1933).

Dem. 57—Combustion of a Candle

To show: Formation of carbon dioxide from a burning candle.

Materials: See Figure 57. A 2-oz square, narrow neck bottle is inverted in a tray of limewater. Inside the bottle a candle is supported on a metal base, candlestick in shape.

Procedure: Light the candle, set it in the tray of limewater, and quickly invert the bottle over it. After the candle goes out, shake the bottle, still holding its neck under the limewater.

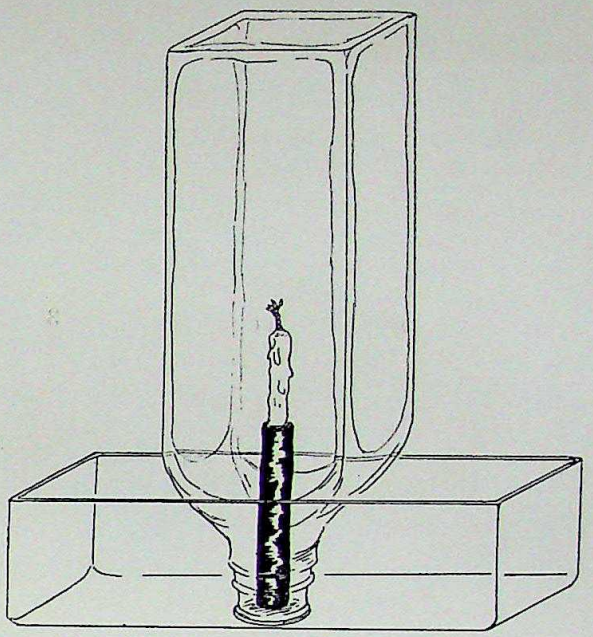


Figure 57. Combustion of a Candle.

Observations: The candle soon goes out when there is still 16% oxygen in the bottle. The water rises up slightly, but not one-fifth. Upon shaking the bottle, the CO_2 which has been formed reacts with the limewater, precipitating calcium carbonate.

Dem. 58—Combustion Products of an Alcohol Burner

To show: Formation of H_2O and CO_2 in burning alcohol.

Materials: Alcohol burner, 40 mm glass funnel, rubber tubing, ice, Schwartz drying tube. This latter is a U-tube 10 cm high, of 18 mm diameter glass tubing, the ends stoppered, and two side-arms of 6 mm tubing.

Procedure: Attach the funnel to the U-tube via a 1-ft length of rubber tubing; to the other arm of the U-tube attach another foot-length of rubber tubing. Immerse the U-tube in a beaker of ice water for a minute. Remove and quickly wipe off all water; act quickly before the cold tube warms up. (*a*) Holding the tube in the projector, focus it so the sides of the tube are clearly seen. Now suck in one breath of air through the funnel. (*b*) Place the lighted alcohol burner on top of the projector where the class can see it. Holding the tube in the projector, hold the funnel over the flame and suck in a single breath. (*c*) Run 2 ml of limewater into the U-tube, and suck the combustion products through it about ten times.

Observations: (*a*) Sucking in ordinary air will produce no change in the tube. (*b*) Sucking in the combustion products from the flame deposits almost instantly a thick layer of moisture. (*c*) CO_2 in the combustion gases precipitates $CaCO_3$.

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Notes: 1. Perform operation (*a*) to establish that thermometer did not come from the air.

2. An 18 mm tube works better than a 8 mm U-tube since there is a greater volume of combustion products to furnish moisture.

3. A gas-washing bottle, shown in SD-8 can be used in place of the U-tube. However the bottle must be left in the ice-water longer to bring it to a low temperature. Device SD-8 is better than the U-tube for the test with limewater.

3. OTHER COMBUSTION PHENOMENA

Dem. 59—Kindling Temperature

To show: Different kindling temperatures for phosphorus, kerosene, and hydrogen.

Materials: CARE. DANGER WITH WHITE PHOSPHORUS, see Dem. 45. White phosphorus, CS_2, 2-in. square of tissue paper, kerosene, Grand Canyon cell H-4, plastic box about $1\frac{1}{2} \times 1\frac{1}{2} \times 1$-in. high, SD-6 cannon or a miniature 3-in. high bottle, hydrogen, oxygen, leak-tester Telsa coil.

Procedure: (*a*) Crumple up the tissue paper and place on asbestos on H-4. Now add a single drop of P in CS_2 (prepared according to instructions in Dem. 45) to the paper (CARE). (*b*) Fill the plastic box with kerosene. DANGER: do not use gasoline. Place on stage and project. Light a splint and thrust it into the kerosene. Remove the box to a square of asbestos on the lecture table and attempt to ignite the kerosene with a bunsen burner. Finally soak a piece of paper in kerosene, place it on the asbestos, and ignite with a match. (*c*) Fill the cannon or miniature bottle with two volumes of hydrogen and one of oxygen. Place on the stage and ignite with the leak tester.

Observations: The kindling temperatures vary greatly. (*a*) Phosphorus ignites spontaneously at room temperature. (*b*) Kerosene is difficult to ignite below 400°C. (*c*) Hydrogen-oxygen mixtures must be heated above 550°C. before explosion occurs.

References: FINE, I., *J. Chem. Educ.*, **8**, 929 (1931).

Dem. 60—Spontaneous Combustion of Oils

To show: Oil mixtures heating up spontaneously in air.

Materials: Cotton or rags, turpentine, linseed oil, Japan drier, forceps, cell M° −1.

Procedure: In a 250 ml beaker mix 10 ml linseed oil + 2 ml turpentine + 2 ml Japan drier. Push a ball of cotton about fist-size into this mixture; remove from the beaker, and knead and squeeze the cotton until it is thoroughly and evenly impregnated with the mixture. Pack this snugly around the bulb of the gas thermometer M° −1. Or, the cotton can be packed into the plastic box of M° −1, around the gas bulb. Set on the stage and project.

Observations: The temperature of the cotton rises rapidly, about ten degrees in 20 minutes. At the end of half an hour remove the oily cotton and pass around the class; the material is surprisingly warm.

Reference: MORRIS, S., AND HEADLEE, A. J. W., *J. Chem. Educ.*, **10**, 637 (1933).

Note: With just turpentine and cobalt drier, without linseed oil, I did not get the temperature rise. See ANTLEMAN, M., *J. Chem. Educ.*, **30**, 134 (1953).

Dem. 61—Shock-tube Rings

This demonstration was suggested by and developed by Robert Groescholl and his teacher, Morris Hutchison, of the Everett, Washington, High School working with the author at the U. S. Science Exhibit, Century-21, Science Theater Laboratory, Seattle, Washington, 1962.

To show: Formation of shock-tube rings during an explosion.

Materials: CS_2, hypodermic needle, stoppered 18 × 180 mm test tubes, small corks to fit inside the tube.

Procedure: Insert a small cork in a tube, then inject a few drops of CS_2 from the hypodermic needle (an ordinary dropper gives drops which are too large). Stopper. Shake the small cork back and forth for a minute to mix the gases; this mixing is more difficult than is realized. Unstopper and bring to a flame. Project the result.

Observation: Violent pop. Over half-a-dozen parallel rings of sulfur may form along the tube, due to shock waves set up. The striations can be clearly projected.

Notes: *1.* Rings do not form every time; it may be necessary to repeat several times, trying different numbers of drops and different sized tubes.

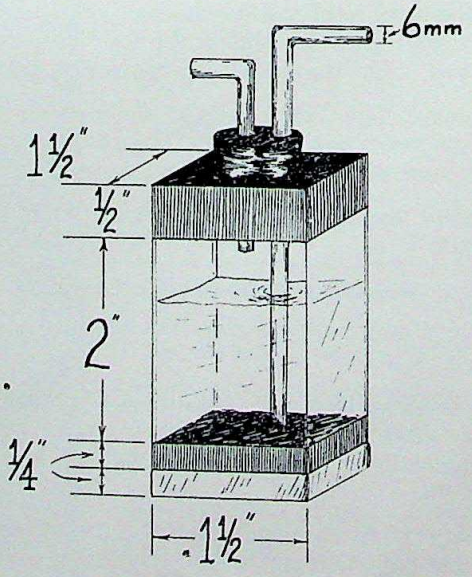
2. Shock-tube research, including problems of standing waves as in a Kundt Sound Tube, is important in a world of supersonic travel.

SUPPLEMENTARY DEVICES

SD-8—Gas-Washing Bottle

The figure is self-explanatory. A bottle about 3 in. high projects satisfactorily. The stopper is rubber, the tubes plastic.

Typical uses: (*a*) Blow through limewater. The CO_2 in the breath precipitates $CaCO_3$. (*b*) Lead H_2S generated in cell G-4 into Pb^{++} solution in SD-8. Black PbS forms. (*c*) Suck the combustion products from a burning candle or alcohol burner through limewater in SD-8. Calcium carbonate precipitates.



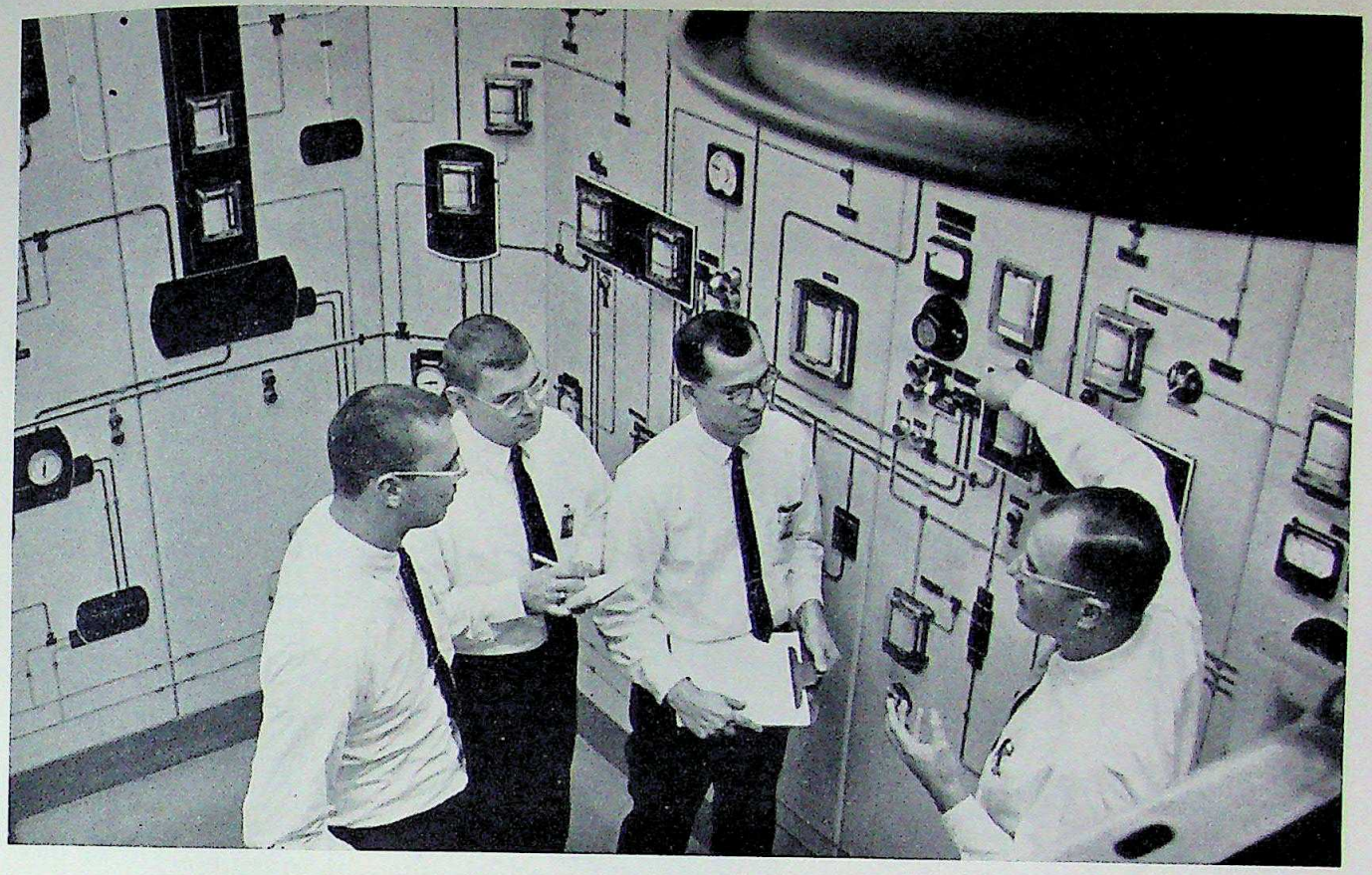
SD-8.

(*To be continued in March*)

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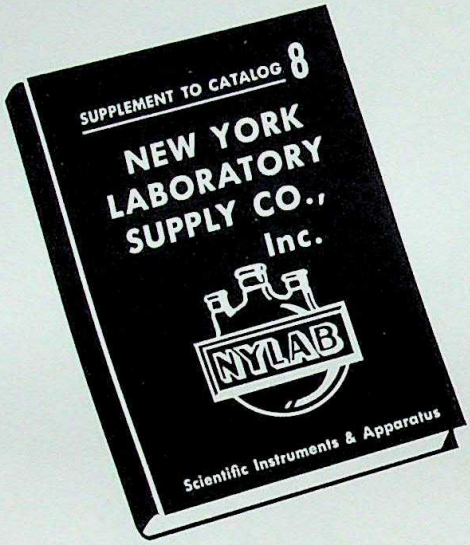
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a ChemEd feature

CHEMICAL PROJECTS

Research Ideas for Young Chemists

Compiled by **JAY A. YOUNG**, King's College, Wilkes-Barre, Penna.
JOHN K. TAYLOR, National Bureau of Standards, Washington, D. C.

Variation in Reactivity—A Demonstration

See BOWEN, D. M., *J. Chem. Educ.*, 26, 330 (1949).

Isomers with the same empirical composition often exhibit substantial differences in their chemical properties. Similarly, widely separated members of a homologous series show marked differences. A series of three experiments with normal and with tertiary-butyl bromide is described, illustrating this fact. These involve the replacement of the Br, in each isomer, with I, with NO_3, and with OH. The reactivities of the two isomers are not comparable in all three experiments.

Questions:

Find two other isomeric compounds which show differences in their reactivities with various reagents which you select. Experiment 28 in the 2nd edition of the CHEM Study laboratory manual illustrates another type of isomeric effect on reactivity.

Is it true that in a homologous series, the properties of the members of the series show a gradual variation, as the molecular weight increases with each CH_2 unit?

Account for differences you observe in the properties of two isomers, or in the members of a homologous series. Devise laboratory tests to verify your explanation.

The Direct Reactions of Solids

See FEIGL, F., ET AL., *J. Chem. Educ.*, 21, 18–24, 32 (1944).

In this article, fourteen different reactions all of which take place in the absence of a solvent are described. Some of the reactions are unique, and others represent types of reactions with different possible variations (many of which are suggested by the authors).

Typical examples of the fourteen different reactions are, the reaction between magnesium oxide and any one of several metal sulfates, the formation of complex compounds, the reaction between basic and acidic oxides, the decomposition of copper(I) iodide by a catalyst, and the reaction between mercury(II) iodide and copper(I) iodide or silver iodide.

Few papers which have been discussed in this series will suggest as many different ideas for investigations to interested, competent students as this paper. It is truly full of provocative suggestions for students who wish to study chemistry and who seek challenging suggestions for their own laboratory investigations. Most of the suggested experiments are easily performed, requiring only a burner and a crucible. However, to answer the question suggested below, other equipment of the sort commonly found in most elementary laboratories will be needed. For thorough investigations, of course, sophisticated instruments will be helpful, though probably not essential.

Question:

Select any reaction explicitly mentioned, or indirectly suggested, in the article. Carry out the reaction and determine by quantitative measurements the balanced equation which describes the reaction you have chosen for study.

Demonstration of Some Properties of Prussian Blue

See KOHN, M., *J. Chem. Educ.*, 20, 198 (1943).

Prussian blue, $Fe_4[Fe(CN)_6]_3$, can be reduced to iron(II) hexacyanoferrate(II), $Fe_2[Fe(CN)_6]$ by hyposulfurous acid, $H_2S_2O_4$. An acidified solution of sodium hyposulfite furnishes the necessary hyposulfurous acid. The reaction is rapid and complete, and the change from a blue insoluble substance to a white insoluble substance is striking. Further, Prussian blue will react metathetically with many substances which contain ligand donors, such as potassium oxalate. In this case, two soluble compounds, tetrapotassium hexacyanoferrate and tripotassium trioxalatoferrate are formed.

Questions:

Can you determine the reactions which occur when Prussian blue is reduced by hyposulfurous acid?

What other reducing agents will reduce Prussian blue to iron(II) hexacyanoferrate(II)? Determine the reactions which take place when a different reducing agent is used.

How many oxidizing agents can you find which will oxidize iron(II) hexacyanoferrate(II) to Prussian blue? Can you suggest a plausible reaction scheme to account for one of these oxidations? Show that such a scheme is or is not plausible, by further laboratory work.

As noted in the article, the iron(III) ion of Prussian blue will accept ligands, such as the oxalate ion, in place of the hexacyanoferrate(II) ligand, with which it is associated in Prussian blue. What other ligands, in addition to the oxalate ion, can you find which will displace the hexacyanoferrate(II) ion from Prussian blue?

(*Continued on page A139*)

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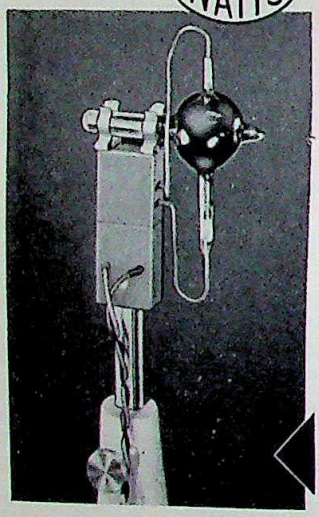
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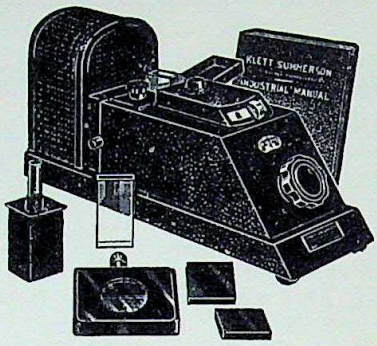
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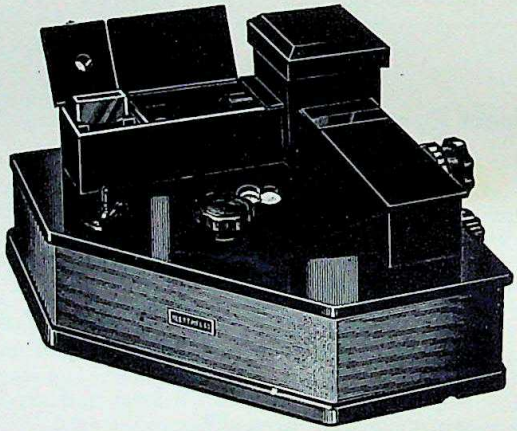
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SEPHADEX cation exchangers, the high-capacity exchangers derived from SEPHADEX, are now commercially available. These new ion exchangers were developed by Pharmacia of Uppsala, Sweden. Under extensive testing, SEPHADEX ion exchangers exhibited the following properties: High capacity for large molecules ■ Low nonspecific adsorption ■ Quantitative desorption ■ High flow rate ■ Good reproducibility ■ Easy column packing

These new products include both weak and strong cation exchangers. CM-SEPHADEX is the carboxymethylether of SEPHADEX. SE-SEPHADEX is a sulfoethylether derivative.

They are produced in two types, C-25 and C-50, thus providing selectivity in the degree of porosity; i.e., cross-linkages. These forms of SEPHADEX are available as a powder in three particle sizes—coarse, medium and fine. Due to their porous structure and high degree of substitution, CM-SEPHADEX and SE-SEPHADEX have a high capacity for large molecules. They show a low nonspecific adsorption, therefore are ideal for chromatography of labile substances such as enzymes and hormones. Relative capacities of these two SEPHADEX cation exchangers are as follows:

ADSORPTION CAPACITY FOR HEMOGLOBIN[1]

SEPHADEX ion exchanger	Type	Hemoglobin capacity
CM-SEPHADEX	C-25	0.7 g./g.
CM-SEPHADEX	C-50	4.7 g./g.
SE-SEPHADEX	C-25	0.7 g./g.
SE-SEPHADEX	C-50	2.4 g./g.

[1]The solution was equilibrated at pH 6.5 in a sodium phosphate buffer (ionic strength 0.05)

PHYSICAL AND CHEMICAL CHARACTERISTICS

The matrix in SEPHADEX ion exchangers consists of cross-linked dextran chains, where the functional groups are attached at random by ether linkages to the glucose residues in the polysaccharide chains.

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- Insolubility in water, yet with pronounced hydrophilic properties that produce rapid swelling
- Varying degree of swelling depending on differences in degree of cross-linkages
- Uniform functional group distribution, both on the inside and outside of gel particles

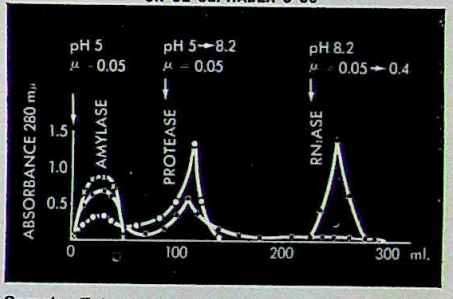
By variation in degree of cross-linkages, different porosities of the network are obtained.

All ionic groups of C-25 and C-50 are available as adsorbing sites. In the C-25 types, molecules less than 10,000 in molecular weight are accessible to all adsorbing sites, although the larger molecules adsorb only on the surface.

SE-SEPHADEX functional groups are strongly acidic and completely dissociated at pH 3. This cation exchanger has a full capacity even at very low pH values, and its exchange capacity is 2-2.5 meq/g.

The fractionation shown below exemplifies many of the purifications possible by an SE-SEPHADEX system:

FRACTIONATION OF ENZYMES IN A PANCREAS EXTRACT ON SE-SEPHADEX C-50



Sample: Extract of pancreas powder with phosphate buffer pH 5.0, $\mu = 0.05$, containing 0.002 M $CaCl_2$.

Elution: Sodium phosphate buffer pH 5.0, $\mu = 0.05$. Then with the same buffer but gradually increasing pH from 5.0 to 8.2, and finally with an ionic strength gradient up to $\mu = 0.4$ at constant pH 8.2. All buffers contain 0.002 M $CaCl_2$.

CM-SEPHADEX is most effective at pH values above 4-5, and the very high exchange capacity of 4-5 meq/g identifies this cation exchanger as exceptionally suitable for protein chromatography.

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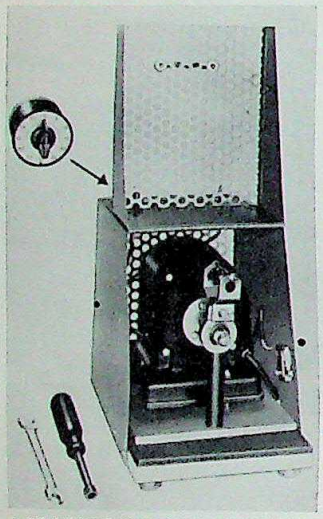
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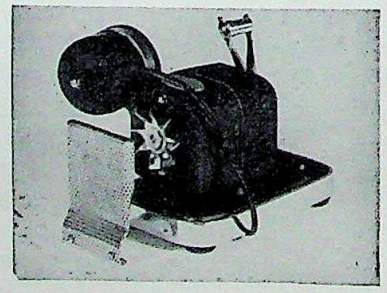
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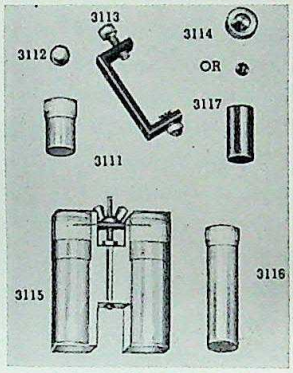
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(continued from page A135)

The Use of the Perkin Reaction in Organic Chemistry Classes

See BUCKLES, R. E., *J. Chem. Educ.*, 27, 210–11 (1950).

In the presence of a base, an aromatic aldehyde will condense with an aliphatic acid anhydride to form an unsaturated acid, Classically, the base used is the anion of the salt of the acid which corresponds to the acid anhydride. However, other bases can be used instead of this anion.

Three examples of the Perkin reaction, using triethylamine as the base, are described. Procedures for the preparation of cinnamic acid, coumarin, and alpha-phenylcinnamic acid are given in detail.

Questions:

Select a compound which you propose to prepare by the Perkin reaction and carry out the synthesis using triethylamine or other base instead of the anion corresponding to the acid anhydride.

Compare the relative efficiency, in terms of rate or of yield, of various bases which are suitable for use in the Perkin reaction. Suggest reasons for the differences in effectiveness you observe and test your explanations by further laboratory work.

Some years ago it was not known whether the aldehyde condensed with the salt of the acid which was present or with the acid anhydride which was also present. Today, it is believed that the aldehyde condenses with the acid anhydride after it has, in a prior step, donated a proton to the base. Can you devise a series of experiments which will confirm this opinion?

Small-Scale Experiments for School Classes

See ADAIR, A., *J. Chem. Educ.*, 22, 129–32 (1945)

Almost all experiments which ordinarily involve the use of gram quantities of reagents and solutions can be modified so that fractional gram quantities suffice. For ease of handling, however, procedures such as filtration, evaporation, decantation, distillation, and others, are performed using modified pieces of apparatus which are superficially different in appearance from familiar pieces of apparatus. Construction of the modified apparatus is interesting; and for students with an inventive turn of mind, construction of other original pieces of apparatus for special purposes, and the use of such pieces, is challenging. Adair describes several modified pieces of apparatus and suggests eight different experiments (for example, the reduction of carbon dioxide by carbon, the preparation of iron(III) chloride, the preparation of copper(II) sulfate) using this small scale apparatus.

Question:

Construct one or more pieces of apparatus described by Adair, or devise your own modifications, and carry out preparative experiments similar to (or identical with) those suggested by Adair.

NOTES: Students who like to design and construct apparatus will find this project particularly interesting. Ideas for experimental investigations which might be modified for small scale work can be found in laboratory manuals; the possibilities are almost limitless, particularly for students who devise their own special modifications of common apparatus for their own special experimental requirements. Adair mentions that an oxygen-gas flame is needed in order to work the borosilicate glass which is used in the apparatus he describes. Be sure, before you begin your work, that you know, and resolve to follow, the safety precautions which apply to the use of cylinders of compressed gas.

Consult indexes of THIS JOURNAL for other references to special equipment devised for handling small scale reactions.

An Amperometric-Kinetic Experiment Emphasizing the Importance of Error Treatment

See YOUNG, J. A., AND ZETO, R. J., *J. Chem. Educ.*, 35, 148–8 (1958).

Nitroethane reacts rapidly with hydroxide ion. If the initial concentration of nitroethane in solution is high, so that only a small fraction of the total amount present reacts within a short time, the concentration of this species can be treated as though it is constant for several minutes. Within this approximation, the rate of the reaction then depends only upon the concentration of hydroxide ion. Hydroxide ion can be formed electrolytically at a known rate equal to its rate of consumption in the reaction. The rate constant of the reaction can be evaluated when these factors are controlled. A mathematical study shows that the calculated value of the rate constant will be strongly dependent upon a measured exponential parameter, the *p*H of the solution. Therefore, the value of the rate constant is very sensitive to errors in the measurement of this parameter.

A cation exchange resin is used to prevent hydronium ion, also produced when hydroxide ion is formed, from entering the solution. The accepted value of the rate constant, 350 l/mole min. at 25°C, is readily obtained, within experimental error. Treatment of the data shows that estimates of the experimental error, obtained with the help of calculus, correspond to similar estimates obtained by the application of ordinary arithmetic.

Questions:

Show that your estimate of the experimental error in the value of the rate constant, obtained by the use of calculus, is consistent with the standard deviation of the rate constant, obtained by arithmetic manipulation of the data from several runs.

Determine the energy of activation of the reaction between nitroethane and hydroxide ion. (Note: The glass electrode of the *p*H meter can be damaged if the temperature of the solution exceeds 60°C.)

Can the rate constant of this reaction be determined if the hydroxide ion concentration is held constant by the slow, controlled, addition of a dilute solution of sodium hydroxide to the reaction vessel?

Why is it necessary to use potassium chloride in the catholyte solution? Would another ionic species be equally satisfactory, or need any salt be present at all?

Is it necessary to use a cation exchange membrane between the anolyte and the catholyte solution?

Other rapid reactions between ions and organic molecules are known. Select one of these for study and determine the rate constant by a modification of the method described in the article.

NOTES: A helical coil of platinum wire can be used in place of the platinum gauze cathode shown in the figure. The coil should be constructed from a piece of platinum wire about 30 cm long, wound to form a helix about 3 cm long, and of 2 cm diameter, centered about the lower end of the anode compartment. Though not shown in the figure, a therometer should be used to monitor the temperature of the catholyte.

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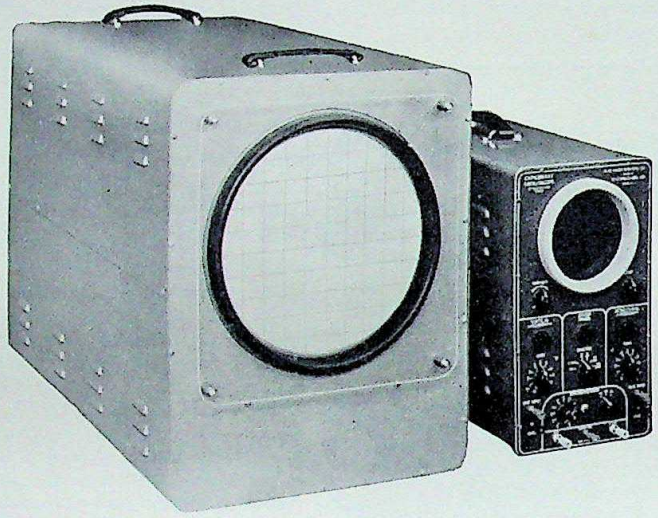
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EDITORIALLY SPEAKING

Silent is not the way for a chemist to be, especially a chemist in the classroom, after reading Rachel Carson's best seller, "Silent Spring." We can be sure that many others whom our students hear will not be silent. Usually those with an axe to grind will speak the loudest. For them a few facts go a long way. Their merging of information into speculation and on to a misconception is hard to detect—especially for students.

"Silent Spring" is not a chemistry book. It is only sometimes a book about chemistry. It is a book dealing with a very important topic in our modern civilization, the use of chemicals, specifically pesticides. The non-chemist often regards the chemistry of pesticides—the structural formulas, the bio-synthetic pathways of metabolism, etc.—as extremely complicated, yet regards the problems of using these chemicals as simple. He may not even heed directions. Even worse, he may, if told only part of the facts by an author of splendid literary accomplishment, be unaware of the fragile foundations on which his opinions are based. There is a tragic similarity between the Twentieth Century thinking which brands the pesticide industry as crassly unconcerned about mankind's welfare and the Middle Ages opinion that Roger Bacon must have been in league with the devil.

Recently the Nutrition Foundation and the Manufacturing Chemists Association have performed a valuable service by providing to a wide mailing list a collection of reviews of Miss Carson's book reprinted from scientific publications. We regard it as very important that these views be made available to all citizens—especially those future citizens now in our classrooms. The following are examples:

Dr. F. J. Stare, Chairman, Department of Nutrition, Harvard School of Public Health, writing in *Nutrition Reviews:*

. . . "Silent Spring" is so selective in the instances Miss Carson chooses to make her points that information the public should know about does not get through to them.

. . . The examples she cites to show the lethal effects of pesticides are all examples of improper use. . . . There never has been one medically documented death due to proper use of insecticides. Deaths due to improper use, says the USDA, totaled 89 in 1961. . . . Aspirin alone accidentally kills about 150 a year, most of them children. No one has suggested that we do away with aspirin—or automobiles which kill thousands.

Dr. W. J. Darby, Head, Department of Biochemistry, Vanderbilt School of Medicine, writing in *C. & E. News:*

. . . Miss Carson's failure to distinguish between the occupational and residue hazards is common to almost all popular writers on this subject. . . . She has not produced one single example of injury resulting to man from these residues.

. . . The July–August 1962 World Health Organization publication reports that a malaria eradication program in Mexico has since 1957 reduced the malarious area from 978,185 sq. km with 18 million inhabitants to 224,500 sq. km with 1.5 million inhabitants. In most areas the simple technique of indoor spraying of house proved effective. . . . As a result of the campaign, the Mexican Government is expanding its agricultural program, distributing land and undertaking irrigation and hydroelectric schemes.

Dr. I. L. Baldwin, Chairman, Committee on Pest Control and Wildlife Relationships, National Academy of Science, National Research Council, writing in *Science:*

. . . Mankind has been engaged in the process of upsetting the balance of nature since the dawn of civilization. . . . Modern agriculture and modern public health, indeed, modern civilization could not exist without an unrelenting war against a return to a true balance of nature.

. . . I suggest as companion reading . . . reports not dramatically written . . . the result of careful study by a wide group of scientists: National Academy of Sciences' Publication 920A and B, "Pest Control and Wildlife Relationships" (1962, $1.25 each); Publication 887, "Use of Chemicals in Food Production, Processing, Storage and Distribution" (1961, $0.50); Publication 470, "Safe Use of Pesticides in Food Production" (1956, $0.50).

. . . Just as it is important for us to be reminded of the dangers inherent in the use of new pesticides, so must our people be made aware of the tremendous values to human welfare conferred by the new pesticides.

The real service to society performed by "Silent Spring" will be lost, if, after the furor it has aroused, complacency returns. The use of chemicals has revolutionized our life. Such revolution does create new problems as well as solve some old ones. Both types need to be recognized, the facts presented, and opinions openly stated. The danger to our society comes when problems, facts and opinions are so scrambled together that all is confused. Helping to set things straight for our students is a difficult job but no chemist in the classroom can avoid it.

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Standard Ionic Crystal Structures

Solid state chemistry involves the formation, motion, and interaction of defects within crystals. An appreciation of these factors involves, as a minimum requirement, a strong intuitive grasp of the structural relationships of the atoms and interstices of various crystal structures. Fortunately this minimum requirement can be readily acquired by limiting one's attention to the small number of idealized ionic crystal structures discussed in this paper. These structures are derived by use of the concept of *the closest packing of spheres* and approximate to varying degrees the actual structures possessed by a large proportion of real crystals. In addition this approach permits one to consider the remaining real crystal structures as being derived from the ideal ones by successively greater deviations from idealized closest packing which in the extreme cases lead to wholesale atomic rearrangements and distortions of the crystal lattices.

The use of the concept of the closest packing of spheres as a key to the intuitive understanding of crystal structures was first suggested by Barlow (*1*, *2*) in 1883, some thirty years prior to the discovery of X-ray diffraction; since that time a number of workers have extended the concept (*3–8*). From this viewpoint crystals are considered to be built up by successively stacking together closest packed monolayers of atoms; the various standard crystal structures then differ from one another mainly in the way in which the interstices between the closest packed atoms are occupied by other atoms. The present approach differs from the former ones in its emphasis on the information to be obtained by carefully considering the relationship between the atoms and interstices first in a single closest packed *monolayer* of atoms and then in a construct of two closest stacked monolayers called a *double layer*. The information so obtained proves to be sufficient to derive all the remaining properties of infinite, three-dimensional constructs of closest packed spheres. In the present paper a qualitative description of this information is presented and applied to the standard ionic crystal structures.[1]

Cubic and Hexagonal Closest Packed Atom Lattices

Infinite, three-dimensional closest packings of spheres of equal size can be considered to built up by the successive stacking together of two-dimensional closest packed monolayers of spheres. The stacking direction is parallel to a cube body diagonal or a ⟨111⟩ direction in cubic closest packing, ccp, and is parallel to the hexagonal rotation axis or [0001] direction in hexagonal closest packing, hcp. The perpendicular separation distance between midplanes of nearest neighbor monolayers is equal to $\sqrt{8/3}r_{cp} = 1.6330r_{cp}$, where r_{cp} is the radius of the closest packed spheres. The spheres of immediately adjacent monolayers fit into three-dimensional hollows of the nearest neighbor monolayers and tangentially contact three spheres of these monolayers. Thus, individual spheres which contact six other spheres in their own monolayer also contact three spheres in each of the two immediately adjacent monolayers leading to the familiar twelve-fold coordination of closest packing. The spheres at the top and bottom of finite, crystal-model representations of closest packed arrays obviously contact a total of only nine neighbors.

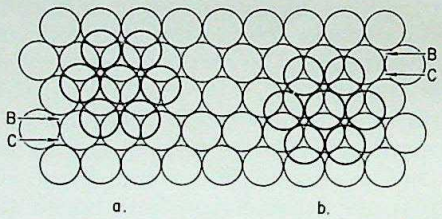


Figure 1. The two possible types of closest packed double layers.

Whenever a new monolayer is added to the topmost layer of a preexisting stack of spheres, a *two fold choice* must be exercised with respect to the manner in which the new monolayer will be added. This two-fold choice is illustrated in Figure 1 and can be stated as follows:

The spheres of the new or upper monolayer (heavy circles in Figure 1) are placed either: *choice a:* exclusively over plane triangular interstices which "point" toward the bottom of the page and which are labeled *B* interstices in Figure 1, or *choice b:* exclusively over interstices which point toward the top of the page and which are labeled *C* interstices in Figure 1.

Figure 1 actually illustrates a single pair of monolayers or a single *double layer* in which the first or lower layer is represented by the light circles and the second or upper layer by the heavy circles. A single exercise of the two-fold choice, which is all that is necessary to construct a double layer, does *not* lead to physically distinct constructs, since either of the two forms of the double layer illustrated in Figure 1 can be converted into the other. For example, rotation by 60° about the the stacking direction perpendicular to the monolayer

This work was carried out under the auspices of the United States Atomic Energy Commission, Contract Number AT-(11-1)-GEN-8, and the paper based upon a portion of North American Aviation –Special Report-6003. The paper was presented at the Pacific Southwest Regional Meeting of the American Chemical Society, San Diego State College, December, 1961.

[1] A detailed mathematical description, "Translation-Permution Operator for the Description of Crystal Structures. I. Ideal Closest Packing," has been submitted to *Acta Crystallographica.*

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midplanes interconverts the two forms as can be seen by simply rotating the page by 60°. Nevertheless, when the two-fold choice is exercised at least twice in succession as it must be to form a closest packed triple layer, it is the *fundamental cause* for the existence of the physically distinct cubic and hexagonal forms of closest packing. The first coordination shell of twelve nearest neighbors of each of these two well-known forms of closest packing is illustrated in an "exploded" fashion in Figure 2; the two structures in the figure are finite fragments of closest packed *triple layers*. Cubic closest packing, ccp, arises from a *perfect repetition* of the same two-fold choice made in forming the initial double layer (spheres X–XII and spheres IV–IX), i.e., either choices $a+a$ or $b+b$. Hexagonal closest packing, hcp, arises from a *perfect alteration* between the two possible choices, i.e., either choices $a+b$ or $b+a$. Futhermore, when the two-fold choice is exercised many times in succession as it must be in forming closest packed multilayers, it is the *fundamental cause* for the possible existence of an infinite number of three-dimensional closest packings. This infinity of additional possibilities (*4*) arises from sequences of this fundamental two-fold choice that are increasingly more complicated than the two simple sequential extremes found in ccp and hcp.

Several other comparative features of ccp and hcp are illustrated in Figure 2. First, the dodecahedral coordination polyhedra inside the cages of nearest neighbor atoms are defined by the intersections of planes perpendicular to and bisecting the connecting lines between the central shaded atom and its twelve nearest neighbors. Second, both the atom cages and the coordination polyhedra illustrate (1) the hcp mirror planes of symmetry which lie in the midplanes

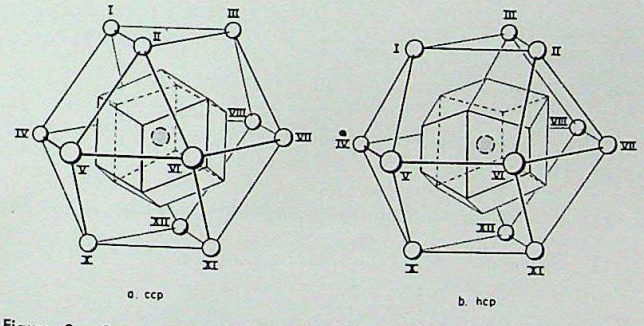


Figure 2. Structure of the first shell of neighbors in cubic and hexagonal closest packing.

of the closest packed monolayers in Figure 2*b*, and (2) the ccp center(s) of symmetry located at the shaded atom in Figure 2a and at all the closest packed atom centers in an infinite three-dimensional ccp array. Third, in studies of the mechanical slip of crystals, hcp is found to have only a single set of closest packed glide planes whereas ccp has four such sets. Thus stacking closest packed monolayers in a ccp fashion automatically generates three other closest packed planes which taken together with the original closest packed plane, form sets of intersecting tetrahedra. The central portions of the faces of the two smallest, intersecting tetrahedra surrounding the central shaded atom in Figure 2*a* are represented by the two sets of triangular interstices (I, II, III) + (IV, V, X) + (VI, VII, XI) + (VIII, IX (not shown), XII) and (X, XI, XII) + (V, VI, II) + (VII, VIII, III) + (IX (not shown), IV, I).

For a first approach to the study of crystal structures one need only concentrate on ideal cubic closest packing, ccp, and ideal hexagonal closest packing, hcp, since the large majority of the crystal structures based on the closest packing of spheres are derived from these two types of packing. However, other types of closest packing do exist in crystals (3–8). In addition, real crystals are usually deformed from perfect closest packing and also have stacking faults or errors in the sequence of twofold choices. But the study of these aspects of crystal structure can be profitably delayed until after the standard crystal structures are mastered.

Interstice Lattices

Of fundamental importance to the effective study of crystal structure is the concept of L. Strock (*9*) that crystal structures are composed not only of lattices of atoms but also of *lattices of interstices*. The three-dimensional interstices lie between the closest packed atoms. These interstices are important since they are the keys to the understanding of the so-called "defect lattices" and of the crystal structures of metal alloys, ionic salts, and minerals.

The three-dimensional interstices are of two types, which can be conveniently described in connection with the models illustrated in Section (*a*) of Figure 3.

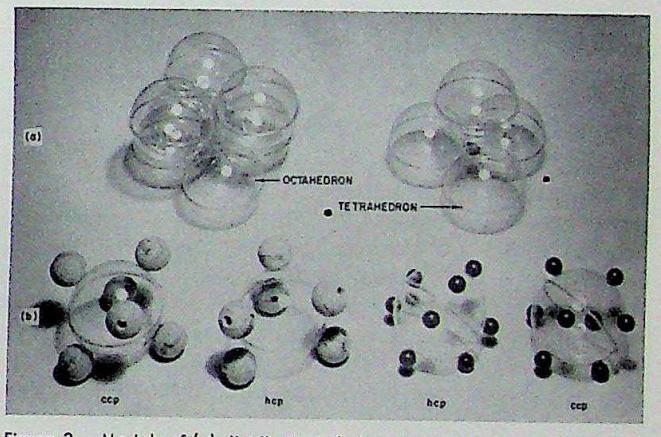


Figure 3. Models of (a) distribution of cloest packed atoms about tetrahedral and octahedral interstices, and (b) distribution of tetrahedral and octahedral interstices about a single closest packed atom in both cubic and hexagonal packing.

Octahedral interstices are enclosed by six closest packed atoms which lie at the apexes of a regular octahedron and by eight plane, curved-triangular interstices that form the faces of the octahedron. *Tetrahedral interstices* are enclosed by four closest packed atoms and by four plane triangular interstices that form the faces of the tetrahedron. If the tetrahedron in Figure 3 is thought of as a three-dimensional arrowhead, the apex of the arrowhead points upward, i.e., in the positive stacking direction or positive z-direction; the tetrahedral interstice defined by such a tetrahedron of closest packed atoms is termed a *positive* tetrahedral interstice and is indicated by the symbol "(+)-tet" where "tet" is an abbreviation for tetrahedral interstice. A tetrahedral interstice defined by a tetrahedron pointing in the negative stacking direction is termed a negative tetrahedral interstice and is denoted as "(−)-tet."

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The three-dimensional interstices are distributed in planes which are perpendicular to the stacking direction and which lie between the midplanes of immediately adjacent monolayers of closest packed atoms. These planes are illustrated in both top and side views in Figure 4 where the tetrahedral interstices are labeled by small plastic spheres and the octahedral interstices by larger cork spheres. The two sizes of spheres representing interstices in Figure 4*a* conform roughly to the tetrahedral radius ratio of 0.225 and to the octahedral radius ratio of 0.414. The vertical coordinate of the plane-of-centers of the interstices, expressed in fractions of the minimum interplanar distance parallel to the stacking direction, is an important characteristic

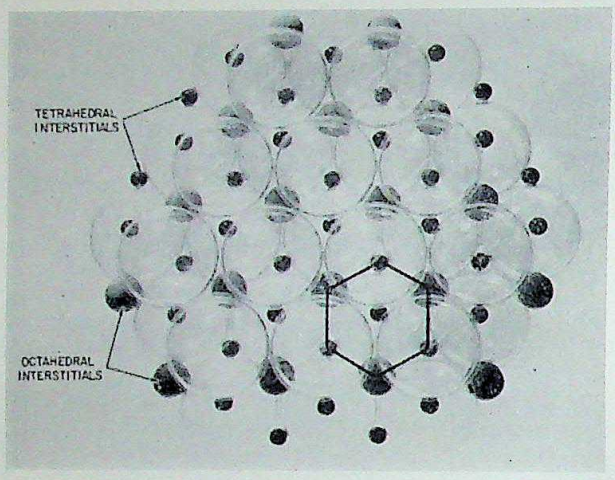


Figure 4a. Closest packed double layer: top view.

of the different interstices. These fractional coordinates are: (+)-tet = $^1/_4$, oct = $^1/_2$, and (−)-tet = $^3/_4$. Due to a slight defect in the construction of the model the (+)-tet interstices in Figure 4*b* appear to be closer to the lower midplane than the correct value of one-quarter of the interplanar distance.

In all closest packed arrays the relative number density of closest packed atoms and three-dimensional interstices is constant and can be expressed by either of two equations:

$$n_{cp} = n_{(+)-tet} = n_{(-)-tet} = n_{oct}$$

$$n_{cp}:n_{tet}:n_{oct} = 1:2:1$$

where n_{cp}, n_{tet}, and n_{oct} are the numbers of closest packed

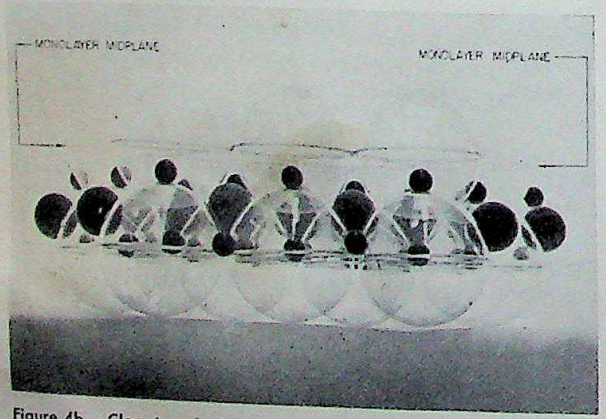


Figure 4b. Closest packed double layer: edge on view.

atoms, tetrahedral interstices, and octahedral interstices respectively, and where $n_{tet} = n_{(+)-tet} + n_{(-)-tet}$. This atom-interstice ratio rule can be derived by considering only the space between the midplanes of two immediately adjacent monolayers as in the double-layer illustrated in Figure 4*b*, and then further restricting attention to a space filling prism within this space such as the hexagon outlined in Figure 4*a*. Since the rule holds at the double layer stage it is independent of any macroscopic symmetry differences among the infinity of closest packing types since these symmetry differences only arise past the double layer stage. Thus the atom-interstice ratio is constant for all closest packings and serves as a key guide to the stoichiometry of compounds with closest packed crystal structures.

A clue to the nature of the interstice lattices in ccp and hcp is supplied by the orientations of the tetrahedral and octahedral interstices around the closest packed atoms in these two types of closest packing. These orientations are illustrated in Section (*b*) of Figure 3 and are also listed below:

ccp: 8 tetrahedral interstices = simple cube[2]
6 octahedral interstices = octahedron

hcp: 8 tetrahedral interstices = complex structure with C_{3h} symmetry,[3] and
6 octahedral interstices = trigonal prism

Particular attention should be paid to the distribution of the complete set of both positive and negative tetrahedral interstices around the closest packed atoms in ccp, a simple cubic arrangement, and the octahedral interstices in hcp, a trigonal prism arrangement. When these two types of units are separately combined together to form three-dimensional arrays, they give rise to the arrangements of tetrahedral interstices and octahedral interstices that can be seen by looking ahead to Figures 8 and 11, respectively. These two arrangements provide the "keys" to the visualization of closest packed structures that can be of great value, either when reading a journal article under such circumstances that textbooks and crystal models are unavailable, or when attending scientific meetings. These "keys" can be stated as follows:

(1) The simple cubic tetrahedral-interstice-lattice is the key to ccp
(2) The simple hexagonal octahedral-interstice-lattice is the key to hcp

For example, Figure 5 illustrates that the tetrahedral-interstice-lattice in ccp forms a three-dimensional checkerboard of simple cubes, half of which are occupied by closest packed atoms and the other half being occupied by octahedral interstices. Figure 10 illustrates that the octahedral-interstice-lattice in hcp forms a peculiar type of simple hexagonal, three-dimensional checkerboard of trigonal prisms, half of which are occupied by closest packed atoms, with the other half being

[2] Note that these 8 interstices are actually split into two sets of 4(+)-tet and 4(−)-tet interstices, each set defining the apexes of a regular tetrahedron, however it is more valuable to ignore the distinction between the two sets in the case of the particular point being presently considered.

[3] C_{3h} symmetry has a threefold rotation axis perpendicular to a mirror plane of reflection-symmetry. The complex structure can be viewed as either two intersecting, twinned regular tetrahedra or as a compressed trigonal prism with a triangular prism on each triangular face.

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occupied by pairs of tetrahedral interstices that are oriented parallel to the *z*-axis.

The Approach of A. F. Wells

The use of the concept of the closest packing of spheres, as a *key* to the intuitive understanding of crystal structures, is best illustrated in the case of ionic crystals. Using a single theme throughout his whole text, Wells (*3*) is able to bring together a myriad of crystal structures into a unified picture. This theme has two parts. First, *the closest packed ions which occupy the bulk of the space in the crystal are picked out.* Second, *the distribution of the remaining ions over the interstice lattices of the closest packed structure is determined.* In one sense, the larger, closest packed ions "determine" the crystal structure, in that

(a) Their structure will be reflected in the macroscopic form of the crystal, and

(b) Their structure determines the symmetry of the interstice lattices, and therefore limits the symmetry of the lattices of the smaller ions.

However, it should be emphasized that the role of the smaller ions (usually the cations) is not entirely passive, but may well be the dominant factor in determining whether the anion structure of strongly ionic crystals is ccp or hcp. The importance of the smaller ions arises from the differing symmetries of the lattices of the interstices in ccp and hcp. This difference can, in certain cases, violate Pauling's Rules (*3*) and lead to extra repulsive forces being present in the hcp structure that are not present in the ccp structure, and which are not compensated by any additional attractive forces. Thus, in these cases, the potential energy, and hence the thermodynamic free energy, of the hcp structure will be higher than that of the ccp structure.[4]

Standard Crystal Structures of Type M_aX_b

The *standard ionic crystal structures* are defined as those structures which (1) contain only two types of ion, (2) possess either a cubic or hexagonal closest packed structure of one of the ions (usually the anions), and (3) have the smaller ions (usually the cations) distributed over the planes of tetrahedral and octahedral interstices in such a manner that all the planes of a given type are either completely occupied or completely empty (but not partially occupied). In the case of the standard crystal structures the first part of the above two-part theme is carried out by simply limiting one's attention to either ccp or hcp arrays of the anions, X. Then in carrying out the second part of the theme, distributing the small cations, M, throughout the octahedral and tetrahedral interstice lattices, two parameters are available: (1) the nature of the interstice occupied, i.e., either small tetrahedral interstices (radius ratio = $\rho = 0.225$) or larger octahedral interstices ($\rho = 0.414$), and (2) the number of the interstices that are occupied. The first parameter depends, to a large extent, upon the radius ratio, but by no means completely on this factor; the electronic configuration of the cation, and the relative polarizabilities of the anions and cations, markedly affect the situation. For example, a classic counterexample is found in the mineral spinel, $MgAl_2O_4$ in which the larger magnesium ions (Pauling radius = 0.65 Å) occupy tetrahedral interstices and the smaller aluminum ions (Pauling radius = 0.50 Å) are in octahedral interstices. The second parameter is determined by the requirement that the crystal, as a whole, be *electrically neutral.*

Applying these two parameters to the 16 combinations of anion and cation charges ranging from ± 1 through ± 4, and selecting relatively simple distributions of the cations over the interstice lattices, leads to the different types of possible crystal structures listed in Table 1.[5] Examples are presented for as many different types as are presently known and listed in the third edition of Wells' text (*3*); it should be noted that in some cases a number of examples are known other than the single example listed and that several of the examples listed exist in more than one crystal form. Not all of the charge combinations are possible in closest packed crystals, and not all the possible cases can be realized without such severe distortions occurring that they destroy any simple crystal symmetry. For example, as frequently noted by Wells (*3*), cations with charges of +3 and +4 have such high ionic potentials—V, where V = (cation charge)/(cation radius)—that they severely distort the electron density of the surrounding anions and tend to form covalent bonds. On the other hand, anions with charges of −3 and −4 are highly polarizable, strongly tend to form covalent bonds, and tend not to exist as simple ions at all. Depending upon the particular combinations of atoms, the directional characteristics of covalent bonds lead either to a molecular crystal structure due to the formation of neutral molecules (e.g., SiF_4) or to complex structures. These complex structures include examples with finite complex ions (such as AlF_4-), infinite chains (as in the silicates), or infinite, three-dimensional structures (such as AlF_3). Thus, the structures to the lower left of the

[4] A paper entitled "Instability of Hexagonal Analogues of Certain Cubic Crystals" is in preparation.

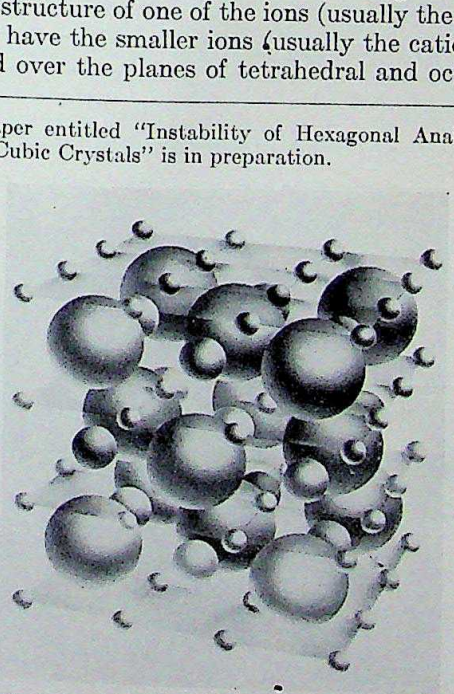


Figure 5. The Li_3Bi structure (note that in Figures 5–9, the positive *z*-axis extends from the lower left front corner to the upper right rear corner of the cubic structure).

[5] Note that the entries in Table 1 are the standard names for the types of structure without regard to the actual ionic charges involved. For example, any ccp structure with a 1:1 ratio of cations to anions in which all the octahedral interstices are occupied, is called an NaCl type of structure; examples of compounds with this structure and varying charges are: ± 2, MgO; ± 3, LaN; ± 4, ZrC (although the last two are more likely of the nature of intermetallic compounds than ionic crystals, since ions of such extreme charges are unlikely, except in gaseous discharges).

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table (below the lower heavy line) and to the upper right of the table (above the upper heavy line) in Table 1 are usually not realized in any simple form. The structures between the two heavy lines contain all the *standard ionic crystal structures*. However, a few of the entries lying between the two heavy lines in Table 1 are exceptions to the definition of a standard crystal structure. For example, the common α-Al_2O_3 structure (corundum) is not a standard structure since the layers of octahedral interstices are only two-thirds occupied and neither completely filled nor completely empty. A more complicated exception occurs in the cases of Al_2Se_3 and Ga_2S_3 where the fraction of tetrahedral interstices occupied is incommensurable with the eightfold coordination of tetrahedral sites around a closest packed atom. In these structures the Group III atoms are considered to be *randomly* distributed over either the set of positive or negative tetrahedral interstices and to occupy each site of the given set with a two-thirds occupation-probability. However, this assumption of a random occupation implies (1) that the system is what is termed an *order-disorder* system (*10*), (2) that the temperature at which the crystal structure was determined was above the order-disorder transition temperature since the disordered state was observed, and (3) that at low enough temperatures, i.e., below the order-disorder transition temperature, an ordered state would exist in which the Group III atoms would occupy fixed positions around the closest packed Group II atoms and lead to a relatively complicated over-all crystal structure.

The Standard CCP Crystal Structures

With the preceding information as background, the chief aim of this paper can be presented quickly; that aim is the development of an "intuitive grasp" of the whole field of crystal structure, which can be gained by an appreciation of the derivation and interrelationships of the standard crystal structures. The approach starts with closest packed arrays of anions which have all their octahedral and tetrahedral interstices occupied by cations, and proceeds by systematically emptying out the cation sites. The ccp case will first be considered, and then the hcp case will be separately considered.

The starting point of the standard structures based on ccp anion arrays is illustrated, in an "exploded" fashion, in Figure 5. The large spheres are the ccp anions, the intermediate sized spheres are the cations in octahedral interstices, and the small spheres are cations in tetrahedral interstices. It should be immediately noted that the least negative charge that the anions can have, in this structure, is -3; since, even with cations of the least positive charge ($+1$) there will be three cations per anion, due to the fundamental ratio of 2 tetrahedral interstices to 1 octahedral interstice per 1 closest packed atom.

(1) *The Li_3Bi Structure.* The structure illustrated in Figure 5 is found for materials such as Li_3Bi, and is called the Li_3Bi structure. The material Li_3Bi is more properly termed an intermetallic compound than an ionic crystal, since the distortion of the structure that would be expected with a highly polarizable -3 anion is absent.

(2) *The NaCl Structure.* The Li_3Bi structure is a relatively uncommon type of standard crystal structure. However, the grandfather of all crystal structure analysis, the NaCl structure, is readily derived from the Li_3Bi structure by simply emptying out all the tetrahedral interstices, to give the result illustrated in Figure 6.

(3) *The $CdCl_2$ Structure.* Then emptying out *one half* of the remaining octahedral sites, by removing

Table 1. The standard crystal structures

Typical Compound	Halide			Oxide			Nitride			Carbide		
Anion Charge	-1			-2			-3			-4		
	Distribution	ccp	hcp	Distribution	ccp	hcp	Distribution	ccp	hcp	Distribution	ccp	hcp
Cation Charge												
+1	all oct	NaCl	?*	all oct + 1/2 tet	?	?	all oct + all tet	Li_3Bi	?	none	XX	XX
	1/2 tet	Z	W	all tet	Li_2O	?*				none	XX	XX
+2	1/2 oct	$CdCl_2$	CdI_2	all oct	NaCl	NiAs	all oct + 1/4 tet	?	?	all oct + 1/2 tet	?	?
	1/4 tet	HgI_2	β-$ZnCl_2$	1/2 tet	Z	W	3/4 tet	anti-Mn_2O_3	?	all tet	?	?*
+3	1/3 oct	$CrCl_3$	BiI_3	2/3 oct	?	α-Al_2O_3	all oct	NaCl	NiAs	(all oct + 1/6 tet)	X	X
	(1/6 tet)	X	$AlBr_6$	(1/3 tet)	Al_2Se_3	β-Ga_2S_3	1/2 tet	Z	W			
+4	1/4 oct	?	?	1/2 oct	?	?	(3/4 oct)	X	X	all oct	NaCl	NiAs
	1/8 tet	SnI_4	?	1/4 tet	SiS_2	?	3/8 tet	?	?	1/2 tet	Z	W

Legend:
- oct An octahedral interstice
- tet A tetrahedral interstice
- Z The ccp ZnS structure, zincblende or sphalerite
- W The hcp ZnS structure, wurtzite
- X Combined with "( )" indicates that the stated fraction is incommensurable with the total number of interstices of the given type (i.e., 8 tet per cp atom and 6 oct per cp atom)
- ? The given type of compound is possible, but not highly likely without severe distortion; and it has not been reported in any simple structure, to date
- ?* Compounds of this type are unlikely, due to excessive coulombic repulsion, in the hcp case
- XX Compounds of this type are impossible, due to electrical non-neutrality

Note Added in Proof: In $+4,-1$ structures the entries "1/4 oct ? ?" should read "(1/4 oct) X X", and in the $+1,-3$ structure the entry under hcp should read "?*".

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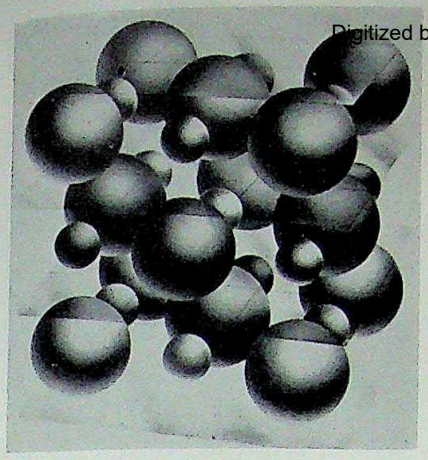


Figure 6. The NaCl structure.

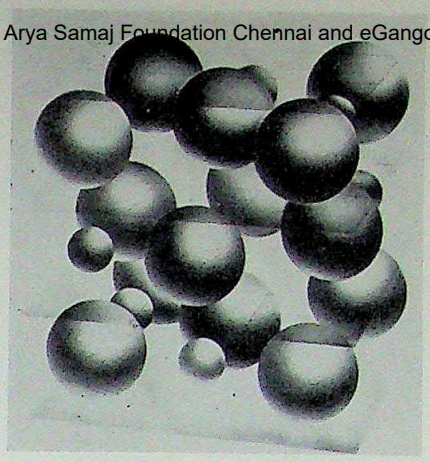


Figure 7. The $CdCl_2$ structure.

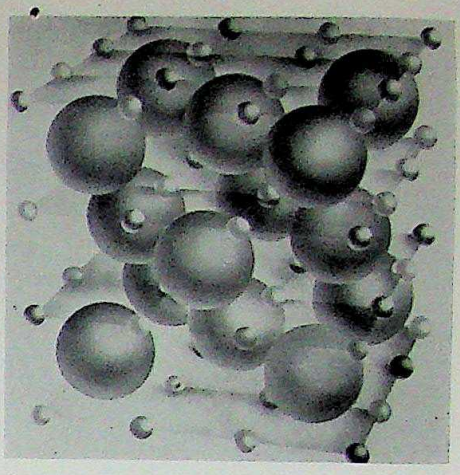


Figure 8. The Li_2O structure.

alternate ⟨111⟩ planes of cations, results in the $CdCl_2$ structure illustrated in Figure 7.[6] A simple rationale of the emptying-out process can be given in terms of the ionic charges: since divalent cadmium has twice the charge of sodium, only half as many cadmium ions are required to neutralize the uninegative chloride ions; this rationale is, of course, implicit in the derivation of Table 1.

(4) *The Li_2O Structure.* If, instead of the tetrahedral sites, *all* the octahedral interstices are emptied, the Li_3Bi structure is converted to the Li_2O structure, illustrated in Figure 8, which clearly exhibits the *key* tetrahedral interstice lattice of the ccp structure.

(5) *The ZnS (Sphalerite) Structure.* Finally, if *one half* of the tetrahedral interstices of the Li_2O structure are systematically emptied out, the cubic zinc sulfide structure of sphalerite is formed (Figure 9). In the figure the (+)-tet positions were *all* emptied out.

[6] This structure is named the cadmium chloride structure, although $CdCl_2$ itself is distorted along a <111> axis to form a rhombohedral structure derived from a cube that has been compressed approximately 3% along the body diagonal.

If, instead of alternate planes of octahedral sites, every plane had one-half its cations removed, each closest packed anion would have three cation neighbors forming a right angle instead of an equilateral triangle, as in $CdCl_2$, and the resulting charge asymmetry causes the hypothetical structure to (undergo a hypothetical phase change and) form the rutile structure.

The Standard HCP Crystal Structures

(1) *The Analogue of the Li_3Bi Structure.* The hcp analogues of these structures can be considered to be derived either by: (*a*) Shifting the ccp anion lattice, in each case, to a hcp structure and moving the cations to the appropriate interstices, or (*b*) Just shifting the ccp Li_3Bi structure to its formally possible hcp structure, and then systematically emptying out the cation sites. Either way, the result is the same; but, for convenience, we shall use the second approach. The hcp analogue of Li_3Bi is illustrated in Figure 10. (Note in Figures 10, 13, and 14, that atoms in tetrahedral interstices that are behind the cp atoms, and would be completely hidden in the figure, have been indicated by being lightly "ghosted-in.") This hcp analogue of a ccp structure does not exist in highly ionic crystals, since there are pairs of cations in both tetrahedral and octahedral interstices that are much closer together than in the cubic case. This leads to electrostatic repulsive forces that render the structure unstable(*11*).

(2) *The NiAs Structure.* The hcp analogue of NaCl, formed by emptying out *all* the tetrahedral

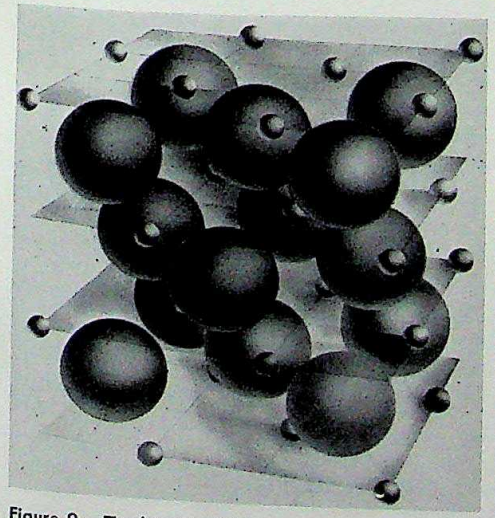


Figure 9. The (zincblende) ZnS structure.

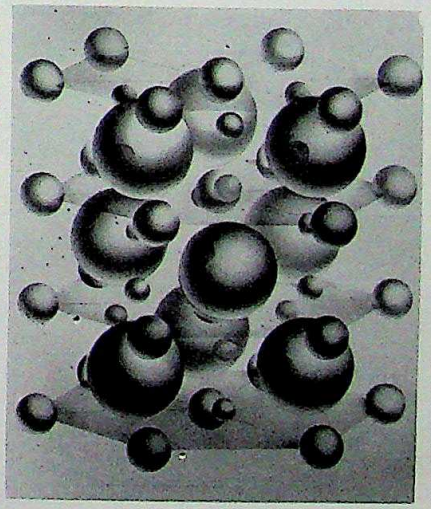


Figure 10. The hexagonal analogue of the cubic Li_3Bi structure.

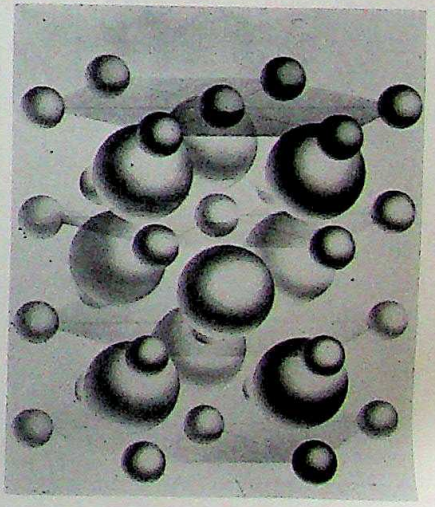


Figure 11. The NiAs structure.

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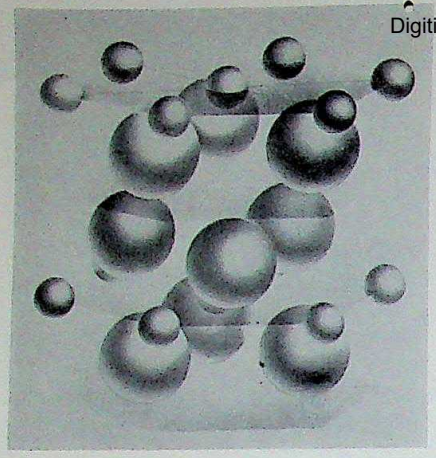


Figure 12. The CdI_2 structure.

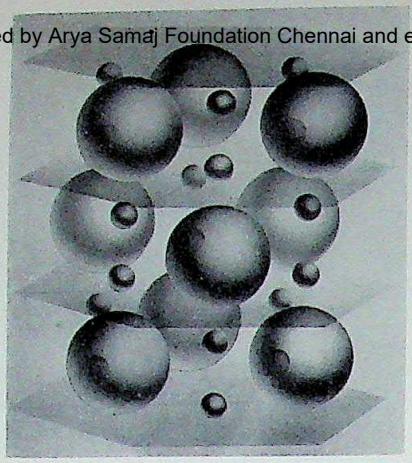


Figure 13. The hexagonal analogue of the cubic Li_2O structure.

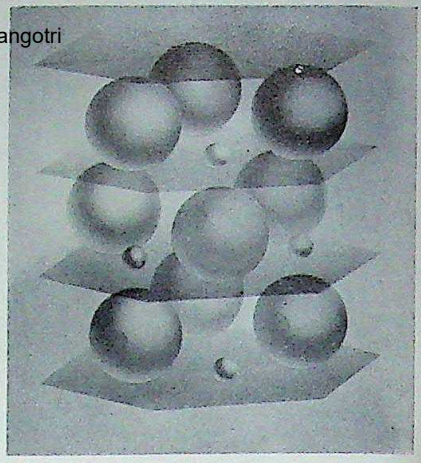


Figure 14. The ZnS (wurtzite) structure.

interstices of the starting hcp structure, is the NiAs structure. It is also not found in highly ionic crystals due to excess coulombic repulsion forces. However, it is observed in (1) such polarizable compounds as FeS, CoS, etc., and (2) in the compound NiAs which is compressed along the c_0 axis to such an extent that the Ni atoms exchange electrons to form what might be termed one-dimensional metal lattices in a matrix of As atoms. Thus, it is only in the case of very polarizable salts, intermetallic compounds, and alloys that the hcp analogues of the ccp structures are expected with the exceptions of the ZnS and CdI_2 structures (see following sections). The NiAs structure, illustrated in Figure 11, clearly exhibits the *key* octahedral interstice lattice of hcp structures.

(3) *The CdI_2 Structure.* Continuing on from the NiAs case, and emptying out *one-half* of the remaining octahedral sites by removing alternate ⟨111⟩ planes, leads to the CdI_2 structure (Figure 12) which is the hcp analogue of $CdCl_2$. Unlike $CdCl_2$, CdI_2 closely approximates ideal closest packing and exhibits a c_0/a_0 ratio of 1.61, compared to the ideal value of 1.633.

(4) *The Analogue of the Li_2O Structure.* The hcp analogue of Li_2O is formed by emptying out *all* the octahedral sites of the hcp starting structure; and, like the parent structure, is also not observed in ionic crystals (Figure 13).

(5) *The ZnS (Wurtzite) Structure.* Finally, emptying out *one half* of the tetrahedral interstices of the hcp analogue of Li_2O leads to the hcp zinc sulfide structure of the mineral, wurtzite, which is considered a standard crystal structure (Figure 14). In this figure the (+)-tet interstices were emptied out.

Deviations from Ideal Closest Packing

The discussion, so far, has illustrated the great usefulness of the concept of closest packed spheres in tying together a great number of diverse crystal structures in a qualitative fashion. However, in a quantitative sense almost all real crystals deviate to some extent from ideal closest packing. In fact, only the 27 face centered cubic elemental metals are truly cubic closest packed, but this circumstance is actually "by definition." Of the 24 nominally hexagonally closest packed metals, three have c_0/a_0 ratios in large excess of the ideal value of 1.6330, five closely approximate the ideal value of the ratio with values of 1.633 ±0.04 but none of these exactly equals 1.6330, and the remaining 16 all have values of the ratio that are markedly less than the ideal value. In the case of the ionic crystals, no example of ideal closest packing is known simply because no cation-anion pair has a rigid-sphere radius ratio of the exact value for either tetrahedral or octahedral interstices. For example, using Pauling radii, the closest fit to the tetrahedral radius ratio of 0.225 is found in BeO, where $(r_{Be^{++}}/r_{O^-}) = 0.31/1.40 = 0.221$. No example closely fitting the octahedral radius ratio of 0.414 is known; two of the closest are found in the cases of LiCl and MgO which straddle the ideal value: $(r_{Li^+}/r_{Cl^-}) = 0.60/1.81 = 0.331$ and $(r_{Mg^{++}}/r_{O^-}) = 0.65/1.40 = 0.464$.

Nevertheless the majority of crystal structures can be considered to approximate to a greater or lesser extent the ideal state exemplified by the ideal closest packing of spheres. Even the silicates can be viewed as consisting of very closely packed triple and quadruple layers of oxide ions and +2, +3, or +4 cations, with the triple and quadruple oxide layers being "spaced" by the presence of relatively large alkali or alkaline earth cations.

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Some Models of Close Packing

Three dimensional sketches of the models in Figures 1 and 2 (or a line lattice equivalent) are often used to represent the difference between *ABABAB* . . . and *ABCABCABC* . . . close packing of spheres. It is readily apparent that *AB* packing gives rise to a

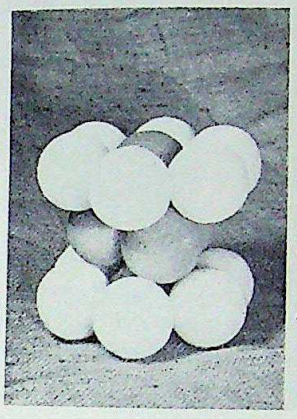


Figure 1.

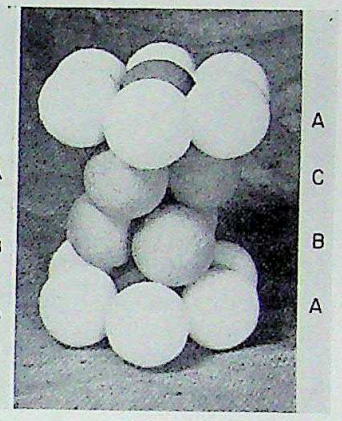


Figure 2.

hexagonal unit cell to which the model in Figure 1 is equivalent.[1] However, it is not immediately apparent that Figure 2 is of cubic symmetry. Both models in Figures 2 and 3 consist of the layers *ABCA*, although three spheres have been added to each of the *B* and *C* layers and six spheres removed from the top *A* layer in Figure 2 to arrive at Figure 3. The face centered cube is easily seen in Figure 3.

The reason that the student sees hexagons in both Figures 1 and 2 is because all the layers in both kinds of packing lie perpendicular to a six fold axis of symmetry. The cube is sitting, not on a square face, but on a body diagonal, which is a six fold axis of rotation. The hexagonal prism is sitting on a hexagonal base. A line connecting the face centering atoms in these faces is also a six fold axis of rotation. So what the student intuitively detects in common with the two kinds of packing is not the hexagonalness, but rather the six fold symmetry axis perpendicular to the direction of packing.

The models were constructed from $1^1/_2$ in. styrafoam balls. The balls in each layer were connected with round toothpicks and the layers were stacked close packed. In order to bring out the symmetry of the packing, some of the balls were colored red or yellow. The layers for constructing the models in Figures 2 and 3 are shown in Figure 5, in their proper relative orientation.

[1] Bunn, C. W., "Chemical Crystallography," Oxford University Press, London, 1945, p. 135. The crystallographer generally finds it convenient to choose one third of the illustrated unit cell as his unit cell.

Examination of the model in Figure 3 reveals that the six yellow spheres (medium grey in the photograph) completely inclose an octahedral hole, while under each red sphere (darker grey in the photograph) lies a tetrahedral hole, formed with the three yellow spheres to which the red sphere is tangent. The models in Figures 3 and 4 differ only in the addition of a few spheres in some octahedral holes. If the small spheres represent cations and the large ones anions (the usual case), then the structure is that of sodium chloride, a general type consisting of cubic close packed anions, containing an equal number of cations in the octahedral holes.

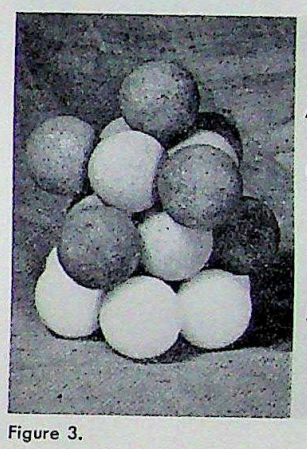


Figure 3.

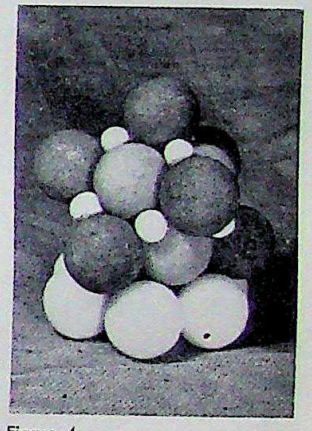


Figure 4.

The coordination number of an ion is the number of nearest neighbors to which it is tangent. In sodium chloride each anion is surrounded by and tangent to six anions; each cation is surrounded by and tangent to six anions, and the structure is 6:6 coordinate. In simple close packing, however, each sphere has twelve nearest neighbors, and is twelve coordinate. If attention is focused on the dark sphere in the top layer in Figure 2, it is seen to be surrounded by six white nearest neighbors. The layer immediately below consists of three more nearest neighbors; immediately above the dark sphere three spheres are missing in the model, for a total of twelve.

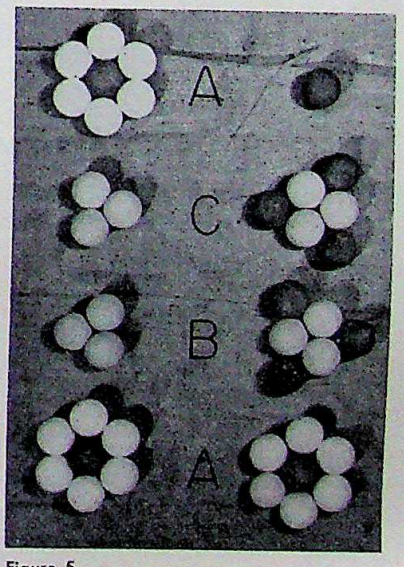


Figure 5.

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The distance between layers in terms of the radii of the spheres may be readily calculated from Figure 6. The centers of four spheres in contact with each other in this close packed manner form a regular tetrahedron, the altitude h of which is the layer separation and is given by: h equals $(s\sqrt{6})/3$, where s is the length of the edge of the tetrahedron. Since the length of the edge is twice the radius of a sphere, the axial ratio $(2h/2r)$ for any hexagonal close packed structure is just $(2\sqrt{6})/3$ or 1.633.

When the centers of four close packed spheres forming a tetrahedron are located on a rectangular coordinate system, they lie on the corners of a cube illustrated in Figure 7. The calculation of the size of a tetrahedral hole is simplified when it is realized that the radius R_c of the hole and R_a of the sphere equals half the body diagonal of the cube whose edge is s. Also, the sum of two radii R_a equals a face diagonal.

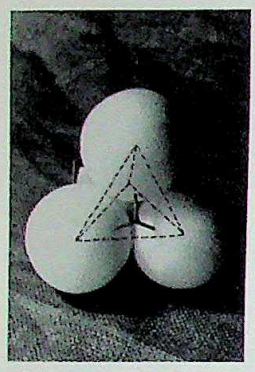


Figure 6.

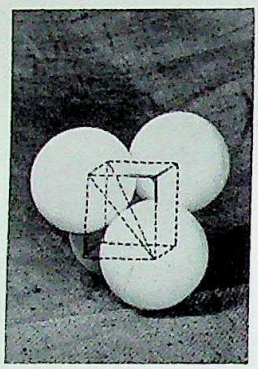


Figure 7.

Thus:

$$2R_a = (s\sqrt{2})$$

And:

$$R_a + R_c = (s\sqrt{3})/2$$

When s is eliminated:

$$R_c/R_a = \sqrt{3/2} - 1 = 0.22475$$

Qualitatively, this ratio is seen in Figure 8, which shows a cation nestled into a tetrahedral depression, the covering sphere having been removed. The size of an octahedral hole in terms of its radius R_c and that of the sphere R_a may be calculated from Figure 9. $\text{Cos}\alpha = R_a/(R_a + R_c) = \sqrt{2}/2$ so that $R_c/R_a = \sqrt{2} - 1 = 0.4142$.

The relative positions and sizes of the spheres, octahedral holes, and tetrahedral holes are shown in Figure 10. The view is parallel to the direction of packing.

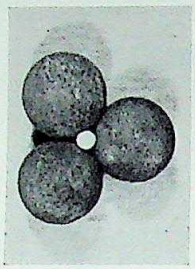


Figure 8.

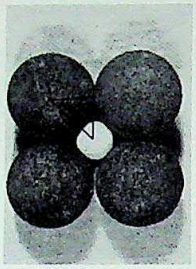


Figure 9.

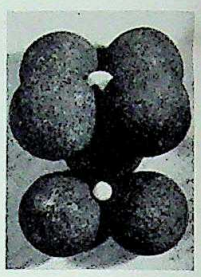


Figure 10.

For a supplementary approach to close packing, the articles by Campbell[2] and by Barnett[3] are helpful. Pauling's monograph[4] contains a wealth of material on close packing, and Sanderson's book[5] is virtually a dictionary of chemical models.

The author wishes to express his gratitude for the support of the National Science Foundation during the period in which this was written.

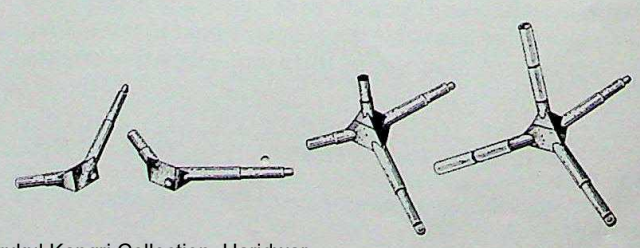
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Sample Models Available for Inspection

A project initiated by Prof. Louis F. Fieser of Harvard University to develop low-cost models for student use has reached the stage where sample models are available for evaluation by a representative of each school that offers courses in organic chemistry. If a school was missed in the first mailing, a faculty member may receive samples by writing Dr. Fieser. Please include an addressed gummed label and indicate the number of sets desired.

The plastic Dreiding model designed by Morningstar Plastics Corp. is constructed as shown in the drawing. Two identical pieces of injection molded polystyrene are cemented together and aluminum tubes are fitted permanently onto the two short rods to complete the assembly. When a plastic rod of one carbon atom is inserted into the tube of another and the two are snapped together, a button near the end of the rod engages with an indentation in the tube and holds the carbons together until pulled apart. A circular to be sent out with sample models gives further details and describes five other simple pieces that complete the set.

The plastic Dreiding model probably will be available at a list price in the range 12–18 cents. An NSF grant defrays the cost of producing and distributing the experimental sample models but does not subsidize production molds and tools.



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Mallinckrodt Uranium Division
Saint Charles, Missouri

Theoretical Titration Error

In potentiometric, asymmetrical precipitation titrations

Kolthoff and Furman[1] and Hibbits[2] have published derivations of the theoretical titration error occurring in potentiometric precipitation titrations. The latter's derivations are based on molar rather than equivalent concentrations and are considerably easier to follow, but in the article titration error is defined as the difference between the concentrations of the substance being titrated at the potentiometric end point and the stoichiometric point. This definition disagrees with that of Kolthoff and Furman[1] and leads to a calculated titration error that is slightly less than half of the correct value for a precipitate of the composition B_2A. For the more general case of the titration of B^{+m} with A^{-n} to form the precipitate B_nA_m, the incorrect definition of titration error leads to such complexities that a general formula for the titration error was not derived in the article by Hibbits. Such a formula is derived below, and a figure is presented showing the magnitude of the theoretical titration error for several types of precipitates. It is shown that the per cent theoretical titration error, for a given amount and kind of precipitate B_nA_m in a given final volume, is independent of whether B^{+m} or A^{-n} is the titrant, and of whether the indicator electrode is sensitive to the concentration of the titrant or to the concentration of the substance being titrated.

Consider the reaction

$$\underset{\text{(titrant)}}{nB^{+m} + mA^{-n}} \rightleftharpoons \underset{\text{(precipitate)}}{B_nA_m}$$

where the potential of the indicator electrode depends on the concentration of the titrant in such a manner that E_A, the difference in potential between the indicator electrode and a suitable reference electrode, is given by the equation

$$E_A = E_A^\circ + k \ln (mx) \tag{1}$$

where E_A° and k are constants when temperature and the activity coefficient of A^{-n} are constant, and mx is the molar concentration of A^{-n}. With this definition of mx (assuming that hydrolysis, complex formation, etc., are insignificant), x becomes equal to the molar solubility of the precipitate for that part of the titration between the formation of a permanent precipitate and the stoichiometric point. For simplicity it will be assumed that activity coefficients, temperature, and volume of the solution remain constant. Even though activity coefficients and the volume of the solution do change during a titration, the changes between the potentiometric end point and the stoichiometric point are so infinitesimal for a practical titration that their neglect will not cause a significant change in the calculated titration error. If

c = initial concentration of B^{+m} and
y = the amount of titrant added divided by the constant volume of the solution,

then after a permanent precipitate has formed, the molar concentration of B^{+m} is

$$B = c - (ny/m) + nx \tag{2}$$

and the concentration solubility product constant for B_nA_m is

$$S = B^n(mx)^m = [c - (ny/m) + nx]^n (mx)^m \tag{3}$$

The potentiometric end point occurs where the second derivative of the electrode potential E_A with respect to the amount of titrant added is equal to zero. At any time after a permanent precipitate has formed, d^2E_A/dy^2 can be found from equations (1) and (3) as follows: Differentiating equation (3) with respect to y and solving for dx/dy yields

$$\frac{dx}{dy} = \frac{n^2x}{m(n^2x + mB)} \tag{4}$$

Differentiating equation (4) with respect to y gives

$$\frac{d^2x}{dy^2} = \frac{n^3xB(m + n)}{m(n^2x + mB)^3} \tag{5}$$

The first and second derivatives of equation (1) with respect to y are:

$$\frac{dE_A}{dy} = \frac{k}{x}\frac{dx}{dy} \tag{6}$$

and

$$\frac{d^2E_A}{dy^2} = \frac{k}{x}\frac{d^2x}{dy^2} - \left(\frac{dx}{dy}\right)^2 \frac{k}{x^2} \tag{7}$$

Substitution of the values for dx/dy and d^2x/dy^2 from equations (4) and (5) into equation (7) gives

$$\frac{d^2E_A}{dy^2} = \frac{kn^3(m^2B - n^3x)}{m^2(mB + n^2x)^3} \tag{8}$$

Since $d^2E_A/dy^2 = 0$ at the potentiometric end point and neither k nor n equals zero,

$$m^2B_p - n^3x_p = 0 = m^2[c - (n/m)y_p + nx_p] - n^3x_p \tag{9}$$

where the subscript p has been added to denote the particular values of B, x, and y at the potentiometric end point. As this equation is equivalent to equation (29) of Hibbits[2] which was derived for an indicator electrode sensitive to the concentration of the substance being titrated, it follows that the potentiometric end point occurs at the same place regardless of whether the indicator electrode is sensitive to the concentration of the substance being titrated or to the concentration of the titrant.

[1] Kolthoff, I. M., and N. H. Furman, "Potentiometric Titrations," 2nd ed., John Wiley & Sons, Inc., New York, 1931, pp. 18–24.

[2] Hibbits, J. O., J. Chem. Educ., 35, 201–2 (1958).

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Since the absolute error in a measurement is generally defined as the measured value minus the true value, the absolute theoretical titration error will be defined as $y_p - y_s$, where y_s is the particular value of y at the stoichiometric point. Thus

$$y_s = mc/n \tag{10}$$

The titration error is readily calculated as follows: From equation (9)

$$y_p = \frac{(m^2 - n^2)x_p}{m} + \frac{mc}{n} \tag{11}$$

and

$$B_p = n^3 x_p / m^2 \tag{12}$$

Substituting the values for x and B at the potentiometric end point into equation (3) gives

$$S = \left(\frac{n^3 x_p}{m^2}\right)^n (m x_p)^m \tag{13}$$

from which

$$x_p = \frac{1}{m} \sqrt[m+n]{S\left(\frac{m}{n}\right)^{3n}}^{3} \tag{14}$$

On subtracting equation (10) from equation (11) and substitution of the value for x_p from equation (14), the absolute titration error is seen to be

$$y_p - y_s = \frac{m^2 - n^2}{m^2} \sqrt[m+n]{S\left(\frac{m}{n}\right)^{3n}} \tag{15}$$

The relative titration error is

$$\frac{y_p - y_s}{y_s} = \frac{m^2 - n^2}{m^3\left(\frac{c}{n}\right)} \sqrt[m+n]{S\left(\frac{m}{n}\right)^{3n}} \tag{16}$$

Since the sign of the charge on B^{+m} and A^{-n} did not enter into the derivation, the equations also hold for the titration of B^{-m} with A^{+n}. In a real titration the volume of the solution does change. The volume that should be used in determining c in equations (10) and (16) is the volume of the solution at the stoichiometric point. Equations (16) shows that relative theoretical error is inversely proportional to c and thus directly proportional to the volume of the solution at the end point.

For the formation of a given precipitate it is of interest to determine what effect the reverse titration, i.e., the titration of $A^{\mp n}$ with $B^{\pm m}$ would have upon the theoretical titration error. In such case the charge on the titrant becomes m instead of n, so that the letters n and m in equation (16) are interchanged; and the initial concentration of the substance being titrated, which is now $A^{\mp n}$, will be denoted by c_A instead of c. With this substitution and after rearrangement equation (16) becomes

$$\frac{y_p' - y_s'}{y_s'} = -\frac{m^2 - n^2}{m^3\left(\frac{c_A}{m}\right)} \sqrt[m+n]{S\left(\frac{m}{n}\right)^{3n}} \tag{17}$$

where the primes have been added to denote the reverse titration. In the case of the same amount of precipitate formed in the same volume of solution, $c/n = c_A/m$ and the relative titration errors are seen to be of equal magnitude but of opposite sign. In either case it can be seen that the potentiometric end point lies on that side of the stoichiometric point where the reactant ion with the lower absolute value of charge is in excess. For example, if $m > n$, so that $A^{\mp n}$ has the lower absolute value of charge, than equation (16) shows that $(y_p - y_s)/(y_s)$ is positive; and thus the titrant, which is $A^{\mp n}$, is in excess at the potentiometric end point.

For the particular case of the titration of B^+ with A^{--} to form the precipitate B_2A, equation (16) becomes

$$\frac{y_p - y_s}{y_s} = \frac{-3\sqrt[3]{S}}{2c}$$

from which the per cent titration error equals

$$\frac{-1.5\sqrt[3]{S}\ 100\%}{c}$$

The absolute value of this per cent titration error does not agree with that calculated by Hibbits[2] who states "that Kolthoff and Furman[1] have presented experimental data with explanatory figures supporting the derivations given." Although an examination of the latter reference did not disclose such experimental data, this book does contain tables[4] and a figure for the titration of silver nitrate with an oxalate solution that were apparently obtained by theoretical calculations. A more or less rough calculation[1] from these tables and this figure gives a theoretical titration error which is in approximate agreement with the original derivations of Kolthoff and Furman[1] and the present derivations but does not agree with the value obtained in accordance with the definition of titration error used by Hibbits.[2]

The reason why titration error should not be called[2] the difference between the concentrations of B^+ at the potentiometric end point and the stoichiometric point can be seen from a consideration of the titration of B^+ with A^{--}. At the potentiometric end point there will be more equivalents of B^+ in solution than equivalents of A^{--} in solution. The amount by which the number of equivalents of B^+ exceeds the number of equivalents of A^{--} at the potentiometric end point may be called the titration error, as was done by Kolthoff and Furman,[1] since this excess of B^+ is equivalent to the amount of titrant needed to titrate from the potentiometric end point to the stoichiometric point. Such a definition does, of course, change the sign of the titration error from that used in the present paper. In order for titration error to be equal to the difference between the concentrations of B^+ at the potentiometric end point and the stoichiometric point, the precipitation would have to be completely quantitative in this region. However, only part—about one-half—of the titrant reacts with B^+ in this region to form a precipitate, and the rest of the titrant merely increases the concentration of A^{--} in solution.

The relative theoretical titration errors are plotted against the negative logarithm of the concentration solubility product S in Figure 1 for several types of precipitates. This figure illustrates the decrease in theoretical titration error that occurs with a decrease

[3] For the case of the electrolyte B_2A, it will be recognized that this equation reduces to $x_p = {}^1/_4\sqrt[3]{S}$. It will be noted that equation 9, page 20, Kolthoff and Furman (footnote 1) which appears to give $x = {}^1/_2\sqrt[3]{S}$ is based on *equivalent* concentrations. It is identical with that here derived for solubility expressed in molar units.

[4] Kolthoff and Furman, *ibid.*, pp. 16–17.

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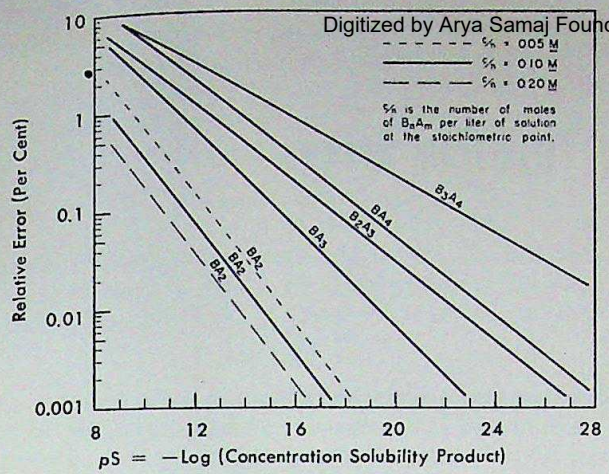


Figure 1. Theoretical potentiometric titration error for the reaction $nB^{+m} + mA^{-n} \rightleftharpoons B_nA_m$ (precipitate). The error is positive if the absolute value of the ratio of the charge on the titrant to the charge on the substance being titrated is less than unity. If this ratio is greater than unity, the error is negative, i.e., the potentiometric end point occurs before the stoichiometric point.

in the solubility product or with an increase in concentration.

If S is known for the ionic strength of the titrated solution at the end point, the per cent theoretical error for any value of c/n may be readily calculated from the expressions in Table 1 for common values of m and n. If S is so small that theoretical error is less than 0.1% relative, a correction will seldom be significant. The values of S at which the relative error is 0.1% for c/n = 0.1 M are given in the last column of Table 1.

If $m = n$, the titration is no longer asymmetrical, and there is, of course, no theoretical potentiometric titration error. Other sources of error, of course, may have to be considered, but are beyond the scope of this paper.

The figure and table presented should enable the analyst to determine readily if a significant theoretical potentiometric titration error exists for a particular precipitate of known S and to calculate the correction if the error is significant.

Acknowledgment

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Table 1. Per Cent Theoretical Potentiometric Titration Error for the Reaction

$nB^{+m} + mA^{+n} \rightleftharpoons B_nA_m$ (titrant) (precipitate)

m[a]	n	$\frac{m^2 - n^2}{m^3(c/n)} \sqrt[m+n]{S\left(\frac{m}{n}\right)^{3n}}\ 100\%$		S in (moles/liter)$^{(m+n)}$ at which % error = 0.1% for (c/n)[b] = 0.1 M
2	1	$\frac{3\sqrt[3]{S}}{4(c/n)}\ 100\%$	$= \frac{75.0\ \sqrt[3]{S}}{c/n}\ \%$	2.4×10^{-12}
3	1	$\frac{8\sqrt[4]{S/3}}{9(c/n)}\ 100\%$	$= \frac{67.5\ \sqrt[4]{S}}{c/n}\ \%$	4.8×10^{-16}
4	1	$\frac{15\sqrt[5]{2S}}{32(c/n)}\ 100\%$	$= \frac{53.8\ \sqrt[5]{S}}{c/n}\ \%$	2.2×10^{-19}
3	2	$\frac{5\sqrt[5]{3S/2}}{18(c/n)}\ 100\%$	$= \frac{30.1\ \sqrt[5]{S}}{c/n}\ \%$	4.0×10^{-18}
4	3	$\frac{7\sqrt[7]{16S/9}}{48(c/n)}\ 100\%$	$= \frac{15.8\ \sqrt[7]{S}}{c/n}\ \%$	4.0×10^{-23}

[a] If m and n are interchanged so that the charge n on the titrant is greater than m, the error is negative, but has the same absolute value.

[b] c/n is the number of moles of B_nA_m formed per liter of solution at the stoichiometric point.

Films on Fluid Mechanics Phenomena

The National Committee for Fluid Mechanics Films is a nonprofit organization of university professors having as their purpose to produce films of experimental phenomena in fluid dynamics. These films are designed to bridge the gap between the conceptual and mathematical aspects of the subject and the perceptual world of the actual phenomena which the theory attempts to model. They are intended as an economical and effective means for supplementing theoretical lectures.

Two films have already been produced: *The Fluid Dynamics of Drag* in four parts of 21, 32, 37 and 29 minutes, purchase price $500 or free loan. It illustrates the drag of streamlined and unstreamlined bodies moving through fluids of low and high viscosity and small and large density. *Vorticity* the second film runs for 44 minutes, purchase price $175 or free loan. Experimental illustrations of the physical significance of the ideas of vorticity and circulation and the related dynamical theorems of Crocco, Kelvin, and Helmholtz are given.

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The cartridge loops, which constitute the second part of the program, are made of 8 mm silent film enclosed in a plastic cartridge and are used with a special projector which is both light and compact. The cartridge loop is inserted into the projector as easily as a book into its place on a shelf, and the film is instantly ready for projection without threading or rewinding. The following loops are currently available: *Shear Deformation of Viscous Fluids, Separated Flows* (Part I and Part II), *Boundary Layer Formation, Generation of Circulation and Lift for an Airfoil, The Magnus Effect, Flow Separation and Vortex Shedding, The Bathtub Vortex, Visualization of Vorticity with Vorticity Meter* (Part I and Part II). The purchase price for each loop is $3.75 and for the projector, $72.50.

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Calculating Titration Errors

Calculating titration errors is one of the most important applications of equilibrium principles to analytical chemistry. Unfortunately, most treatments of this problem have been unsatisfactory from one of two points of view. Either approximations were used which were not valid at the equivalence point, or else the equations obtained rigorously were cumbersome to evaluate. In this paper some explicit expressions for the titration error in acid-base and precipitation titrations will be presented and also a simple method for deciding qualitatively whether or not a given titration is feasible.[1]

The theoretical point in a titration where an amount of titrant exactly equivalent to the amount of substance being titrated has been added is called the equivalence point. The experimental approximation to this, obtained by using a colored indicator or a potentiometric measurement, is called the end point. The difference in volume added between the equivalence point and the end point, divided by the volume added at the equivalence point, is the titration error. The titration error results from the failure to know the exact equivalence point, and is in addition to any errors resulting from volume measurements and weighing.

Symmetrical Precipitation Titration

As an example of a precipitation titration where an insoluble 1-1 salt is formed consider the titration of chloride with silver ion. The same formalism applies to any 1-1 salt such as Hg_2SO_4, $PbSO_4$, AgBr, AgI, AgSCN, etc.

If V_0 ml of chloride ion of molar concentration C_0 is titrated with V ml of silver ion of molar concentration C, the mass balances (*1*, *2*) are

$$[Cl^-] + P = \frac{C_0V_0}{V + V_0} \tag{1}$$

$$[Ag^+] + P = \frac{CV}{V + V_0} \tag{2}$$

where P is the number of moles of AgCl that precipitate per liter of solution. The only equilibrium that need be considered in most of the usual analytical methods (*3*) is the solubility product:

$$[Ag^+][Cl^-] = K_{so} \tag{3}$$

The fraction titrated is defined to be the ratio of the number of equivalents of titrant added to the number added at the equivalence point:

$$\Phi = \frac{CV}{C_0V_0} \tag{4}$$

Note that at the equivalence point, $\Phi = 1$.

Eliminating P between (1) and (2), using (3) to express $[Cl^-]$ in terms of $[Ag^+]$, and using (4) to eliminate CV, we obtain the equation of the titration curve (*4*):

$$(\Phi - 1)\frac{C_0V_0}{V + V_0} = [Ag^+] - \frac{K_{so}}{[Ag^+]} \tag{5}$$

For the purposes of calculating titration error, we can use an approximate relation for the volume factor which applies in the region near the equivalence point. Setting $\Phi = 1$ in (4), we have:

$$\frac{V_0}{V + V_0} = \frac{C}{C_0 + C} \tag{6}$$

When (6) is used to evaluate the volume factor in (5) we obtain the equation for the titration error:

$$\text{Titration error} = \Phi - 1 = \frac{C_0 + C}{C_0C}\left([Ag^+] - \frac{K_{so}}{[Ag^+]}\right) \tag{7}$$

For the reverse titration of silver ion with chloride, the signs of the terms on the right hand side of (7) are reversed.

At the equivalence point, $\Phi = 1$, and (7) gives

$$[Ag^+]^2 = K_{so} \tag{8}$$

which is the equation for $[Ag^+]$ in a solution of AgCl in pure water.

If the concentration of free silver ion at the end point is known, it can be substituted in (7) to obtain the titration error.

Example. In the Mohr method for chloride determination, 50 ml of 0.1 *M* NaCl is titrated with 0.1 *M* $AgNO_3$. As an indicator, 1.0 ml of 0.1 *M* K_2CrO_4 is added. If the end point is taken when the first red precipitate of Ag_2CrO_4 forms, calculate the titration error.

The red precipitate will form when the solubility product of Ag_2CrO_4 is exceeded, that is when

$$[Ag^+]^2[CrO_4^=] \geq 1.1 \times 10^{-12}$$

Since $[CrO_4^=] = 1.0 \times 10^{-3}$, when roughly 50 ml of silver nitrate has been added, the end point will occur when

$$[Ag^+] = 3.3 \times 10^{-5}$$

When this value is substituted in (7), together with $C_0 = C = 0.1$ and $K_{so} = 1.8 \times 10^{-10}$ we get $\Phi - 1 = 5.5 \times 10^{-4}$. This titration error (0.06%) is half the usual buret reading error (0.1%). In practice, the solubility product at a finite ionic strength will be larger than the value given, and an appreciable amount of the red precipitate must form before it is visible. Thus the value calculated represents the minimum possible titration error.

A popular method for determining the end point in a potentiometric precipitation titration is to choose the point where the slope of the titration curve is a maximum. For a symmetrical titration this is the best

[1] This treatment of titration errors will be included in the author's forthcoming book, "Ionic Equilibrium," which will be published early in 1963 by Addison-Wesley Publishing Co., Reading, Mass.

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way of determining the end point, since the point of maximum slope theoretically coincides with the equivalence point. This can be seen by differentiating (7) with respect to pAg ($-\log [Ag^+]$), which gives for the slope near the equivalence point

$$\text{Slope} = \frac{dp\text{Ag}}{d\Phi} = -0.434 \frac{C_0 C}{C_0 + C} \left([Ag^+] + \frac{K_{so}}{[Ag^+]} \right)^{-1}$$

The point of maximum slope occurs where the derivative of the slope is zero. By differentiating the above expression, we find that at the point of maximum slope

$$[Ag^+]^2 = K_{so}$$

This is the same as (8), which gave the value of $[Ag^+]$ at the equivalence point.

Unsymmetrical Precipitation Titrations

For titrations forming unsymmetrical salts, M_2X, such as silver oxalate or mercurous chloride, the titration curve equations are of slightly different form. For the titration of V_0 ml of the divalent ion X of normality C_0 (molar concentration $^1/_2$ C_0), with V ml of the monovalent ion M of molar concentration C, the mass balances are

$$[X] + P = \frac{1}{2} \frac{C_0 V_0}{V + V_0} \tag{9}$$

$$[M] + 2P = \frac{CV}{V + V_0} \tag{10}$$

The equilibrium is governed by the solubility product

$$[M]^2[X] = K_{so} \tag{11}$$

Eliminating P between (9) and (10), and using (11) and (4), we have the equation for the titration curve

$$\frac{C_0 V_0}{V + V_0} (\Phi - 1) = [M] - \frac{2K_{so}}{[M^+]^2} = \frac{K_{so}^{1/2}}{[X]^{1/2}} - 2[X] \tag{12}$$

Near the equivalence point, the volume factor can be approximated by (6), and the titration error is given by

$$\text{Titration error} = \Phi - 1 = \frac{C_0 + C}{C_0 C} \left([M] - \frac{2K_{so}}{[M]^2} \right) = \frac{C_0 + C}{C_0 C} \left(\frac{K_{so}^{1/2}}{[X]^{1/2}} - 2[X] \right) \tag{13}$$

For the reverse titration of a monovalent ion with a divalent ion, the signs on the right hand side of (13) are reversed.

It is well known that the point of maximum slope in an unsymmetrical titration does not coincide with the equivalence point, but explicit expressions for the titration error from this source are not usually given.[2] Such an expression is very simple to derive from (13).

Differentiating (13) with respect to pM gives for the slope

$$\text{Slope} = \frac{dp\text{M}}{d\Phi} = -0.434 \frac{C_0 C}{C_0 + C} \left([M] + 4 \frac{K_{so}}{[M]^2} \right)^{-1} \tag{14}$$

The point of maximum slope is found by differentiating this expression and setting the result equal to zero, which gives the condition

$$[M]^3 = 8 K_{so} \tag{15}$$

The equivalence point, on the other hand, is obtained by setting $\Phi = 1$ in (13), and is at

$$[M]^3 = 2 K_{so} \tag{16}$$

An explicit expression for the titration error from this source is obtained by substituting (15) in (13):

$$\text{Titration error} = \Phi - 1 = \pm \frac{3}{2} \frac{C_0 + C}{C_0 C} K_{so}^{1/3} \tag{17}$$

The positive sign applies for the titration of a divalent ion with a monovalent ion, and the negative sign applies for the titration of a monovalent ion with a divalent ion.

This expression should prove useful in practical potentiometric analysis because the error introduced by taking the end point at the point of maximum slope can be corrected for.

Example. In the titration of 0.005 M Pb^{++} ion with 0.01 M IO_3^- ion, since $K_{so} = 2.6 \times 10^{-13}$, the titration error calculated from (17) is + 1.9%. If the correct end point volume is desired, 1.9% must be subtracted from the volume at which the maximum slope occurs.

In applying (17) in practice, it must be remembered that K_{so} is the concentration equilibrium constant, which holds at the ionic strength of the solution at the equivalence point.

Acid-Base Titrations

The titration of a strong acid with a strong or weak base and the titration of a strong base with a strong or weak acid, can all be considered as special cases of the titration of a weak acid with a weak base. We shall derive an expression for the titration error in a weak acid-weak base titration, and then simplify to give the other cases (*5, 6*).

If V_0 ml of an acid HA of molar concentration C_0 is titrated with V ml of a base B of molar concentration C, the mass balances are

$$[HA] + [A^-] = \frac{C_0 V_0}{V + V_0} \tag{18}$$

$$[BH^+] + [B] = \frac{CV}{V + V_0} \tag{19}$$

There are three equilibria involved in this system:

$$[H^+][A^-] = K_a[HA] \tag{20}$$

$$[H^+][OH^-] = K_w \tag{21}$$

$$K_b[H^+][B] = K_w[BH^+] \tag{22}$$

The final relation required is the charge balance, or electroneutrality condition (*1, 2*):

$$[H^+] + [BH^+] = [OH^-] + [A^-] \tag{23}$$

Eliminating [HA] between (20) and (18) gives

$$[A^-] = \frac{C_0 V_0}{V + V_0} \left(\frac{K_a}{K_a + [H^+]} \right) \tag{24}$$

Eliminating [B] between (22) and (19) gives

$$[BH^+] = \frac{CV}{V + V_0} \left(\frac{K_b[H^+]}{K_w + K_b[H^+]} \right) \tag{25}$$

Substituting (21), (24), (25), and (4) in (23) gives the equation for the titration curve:

[2] J. O. Hibbits, J. Chem. Educ., **35**, 201 (1958) gives an expression for this titration error which differs from our result by about a factor of two, because he defines titration error in an unconventional way. See H. L. Christopherson, J. Chem Educ., **40**, 63 (1963) for an alternative derivation which gives the same result as ours.

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$$\Phi\left(\frac{K_b[H^+]}{K_w + K_b[H^+]}\right) - \left(\frac{K_a}{K_a + [H^+]}\right) = \frac{V + V_0}{C_0V_0}\left(\frac{K_w}{[H^+]} - [H^+]\right).$$

This may be rearranged to give:

$$\Phi - 1 = \frac{V + V_0}{C_0V_0}\left(\frac{K_w}{[H^+]} - [H^+]\right)\left(\frac{K_w}{K_b[H^+]} + 1\right) + \left(\frac{K_w}{K_b[H^+]}\right)\left(\frac{K_a}{K_a + [H^+]}\right) - \left(\frac{[H^+]}{K_a + [H^+]}\right) \quad (26)$$

This equation represents an exact solution of the six equations in six unknowns, but is cumbersome to use in this form.

For calculating titration error in practical acid-base titrations certain simplifying assumptions can be made. If we are close to the equivalence point, the volume factor can be approximated by (6). If $[H^+]$ is small compared to K_a yet large compared to K_w/K_b, we can reduce (26) to the simpler form

$$\text{Titration error} = \Phi - 1 = \frac{C_0 + C}{C_0C}\left(\frac{K_w}{[H^+]} - [H^+]\right) + \frac{K_w}{K_b[H^+]} - \frac{[H^+]}{K_a} \quad (27)$$

which will give the titration error for the titration of a weak acid with a weak base under any conditions where a practical end point could be observed.[3] For the titration of a weak base with a weak acid, the opposite signs are taken for all the terms on the right hand side of (27). By differentiation, it can be shown that the point of maximum slope of the titration curve coincides with the equivalence point, so that the maximum slope method can be used for determining the end point under conditions where indicators are inapplicable.

If K_b is very large, we have the titration of a weak acid with a strong base, and the titration error is given by

$$\text{Titration error} = \Phi - 1 = \frac{C_0 + C}{C_0C}\left(\frac{K_w}{[H^+]} - [H^+]\right) - \frac{[H^+]}{K_a} \quad (28)$$

If K_a is very large, we have the titration of a strong acid by a weak base. This titration is usually performed the other way around, so we shall give the expression (from (27) with opposite signs) for the titration of a weak base with a strong acid:

$$\text{Titration error} = \Phi - 1 = \frac{C_0 + C}{C_0C}\left([H^+] - \frac{K_w}{[H^+]}\right) - \frac{K_w}{K_b[H^+]} \quad (29)$$

If both K_a and K_b are very large, we have the titration of a strong acid with a strong base, whose titration error is given by

$$\text{Titration error} = \Phi - 1 = \frac{C_0 + C}{C_0C}\left(\frac{K_w}{[H^+]} - [H^+]\right) \quad (30)$$

As in the case of the precipitation titrations, the equilibrium constants to be used are concentration constants applying at the ionic strength of the solution at the equivalence point. For rough calculations, the activity coefficients can be assumed to be unity, but for more accurate calculations (if these should become desirable for some reason) an empirical activity coefficient expression such as the Davies equation (7) is useful. In aqueous solution at 25°C the activity coefficient of an ion of charge z is given by

$$-\log \gamma = 0.509\, z^2\left(\frac{I^{1/2}}{1 + I^{1/2}} - 0.2\, I\right)$$

where I is ionic strength.

In converting from pH to $[H^+]$ remember that

$$p\text{H} = -\log [H^+]\, \gamma_{H^+}$$

The Sharpness Index

A convenient quantity to deal with in considering titration errors qualitatively in acid-base titrations is the sharpness index, defined to be the magnitude of the slope of the titration curve at the equivalence point (6):

$$\eta = \left|\frac{dp\text{H}}{d\Phi}\right| \quad (31)$$

By differentiating the expressions derived above for the titration curve in the region near the equivalence point, it is a straightforward matter to obtain explicit expressions for the sharpness index.

For the titration of a strong acid with a strong base, differentiation of (30) and application of the equivalence point condition $[H^+]^2 = K_w$ gives

$$\eta = 0.217\,\frac{C_0C}{C_0 + C}\,\frac{1}{K_w^{1/2}} = 2.17 \times 10^6\,\frac{C_0C}{C_0 + C} \quad (32)$$

where the value of K_w at 25°C has been used.

For the titration of a weak acid with a strong base, differentiation of (28) and application of the equivalence point condition $\Phi = 1$ gives

$$\eta = 0.217\,\frac{C_0C}{C_0 + C}\,\frac{[H^+]'}{K_w} \quad (33)$$

where $[H^+]'$ is the value of $[H^+]$ obtained by setting $\Phi = 1$ in (28). If the equivalence point is more basic than $p\text{H} = 8$, the sharpness index is given by

$$\eta = 0.217\left(\frac{C_0C}{C_0 + C}\,\frac{K_a}{K_w}\right)^{1/2} \quad (34)$$

For the titration of a weak base with a strong acid, differentiation of (29) and application of the equivalence point condition $\Phi = 1$ gives

$$\eta = 0.217\,\frac{C_0C}{C_0 + C}\,\frac{1}{[H^+]'} \quad (35)$$

where $[H^+]'$ is obtained by setting $\Phi = 1$ in (29). If the equivalence point is more acid than $p\text{H} = 6$, the sharpness index is given by

$$\eta = 0.217\left(\frac{C_0C}{C_0 + C}\,\frac{K_b}{K_w}\right)^{1/2} \quad (36)$$

For the titration of a weak acid with a weak base, differentiation of (27) under the assumption that both $[H^+]$ and $[OH^-]$ are small at the equivalence point gives

$$\eta = 0.217\,\frac{C_0C}{C_0 + C}\,\frac{1}{[B]'} \quad (37)$$

where $[B]' = [HA]'$ is the concentration of free base or acid at the equivalence point. Using the mass and charge balances (18) through (23), with $CV = C_0V_0$,

[3] If $[H^+]$ at the equivalence point is of the same order of magnitude as either K_a or K_w/K_b, the equivalence point will occur in the buffer region of either the acid or the base.

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and neglecting $[H^+]$ and $[OH^-]$ compared to $[B]$ and $[HA]$, we can obtain

$$\eta = 0.217 \left\{1 + \left(\frac{K_a K_b}{K_w}\right)^{1/2}\right\} \quad (38)$$

For the intermediate equivalence point in the titration of a diprotic acid with a strong base, it can be shown by similar methods that under the assumption that $[H^+]$ and $[OH^-]$ are small compared to $[H_2A]$ and $[A^=]$ at the equivalence point, the sharpness index is given approximately by

$$\eta = 0.217 \left(\frac{K_{a1}}{K_{a2}}\right)^{1/2} \quad (39)$$

where K_{a1} is the ionization constant of H_2A and K_{a2} is the ionization constant of HA^-. Equation (39) breaks down when K_{a1}/K_{a2} is smaller than 10^3, but this is not a situation of practical importance for titrations. Other equivalence points in polyprotic acid-base titrations can be treated analogously.

These various expressions for the sharpness index can be easily evaluated when the equilibrium constants are known, and the value of the sharpness index can be used to give a qualitative or rough quantitative estimate of the error in a given titration.

With an indicator, using no special methods such as color matching, the *p*H at the equivalence point can usually be estimated to within one unit. From (31), this means that if the sharpness index is larger than 10^3, the titration error will be less than 0.1%, and the accuracy of the titration will be governed by the buret-reading errors. An example of such a titration is the titration of acetic acid with 0.1 molar strong base, for which the sharpness index is 2×10^3. Strong acid-strong base titrations, where C and C_0 are larger than 10^{-3} molar, also fall in this class, provided CO_2 is excluded from the solutions.

Using a *p*H meter to determine the end point by finding the point of maximum slope in the titration curve, the *p*H at the equivalence point can be estimated to within 0.1 units. From (31), this means that if the sharpness index is smaller than 10, even the most precise measurements of the end point *p*H will result in a titration error greater than 1%. An example of such a titration is the titration of HCN with 0.1 molar strong base, for which the sharpness index is 10.

It is hoped that the use of the simple equations derived in this paper will clear up some of the mystery surrounding the calculation of titration error and will make it easier for analytical chemists to decide whether or not a given titration is feasible.

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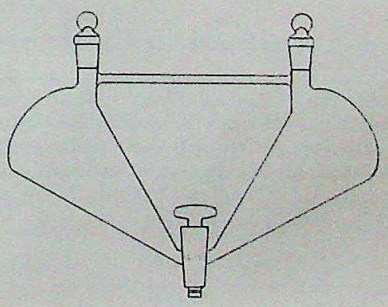
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Separatory Funnel for Successive Extraction of the Heavier Phase

A conventional separatory funnel is inconvenient for re-extraction of the heavier phase, which must be successively run out and returned to the bulb. We have devised a double separatory funnel (see the drawing) which overcomes this inconvenience; it is merely necessary to run the heavy phase back and forth between the two bulbs. The angle of approximately 90° between the two bulbs and the indicated placement of the necks are necessary to allow free flowing of liquid without trapping air while still permitting the utilization of almost the entire volume of the bulbs. Either a solid brace or a vent tube with stopcock may join the necks. As with any separatory funnel, the pear shaped bulbs must taper all the way down to the stopcock if trapping of a small portion of light phase is to be avoided. More versatility could be achieved by extending the principle to three bulbs and a three-way stopcock, but with some unwieldiness resulting. Although the double reparatory funnel was devised for experiments where radioactive contamination, loss of material, or similar problems are involved, it should also prove useful in conventional preparative and analytical procedures.

Acknowledgment. Mr. W. C. Blasky of our laboratory made some suggestions concerning the design and fabricated the first models of the double separatory funnel.



Double separatory funnel for successive extraction of the heavier phase.

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Graphical Treatment Simplifies Acid-Base Equilibria Calculations

In dealing with equilibria involving polybasic acids,[1] considerable simplification of the calculation of the relative distribution of the various species with changes in pH may be obtained by a graphical treatment of the ratios involved.

In the calculation of ratios of the species at a single pH, solution of the appropriate equilibrium expression is simplest and most straightforward,[2] but where numerous computations must be made on the same system, expression of selected ratios in logarithmic form will be found to yield straight lines when plotted as a function of pH, facilitating evaluation of the desired ratios.

Consider the equilibrium relations for a tribasic acid, the dissociation constants of which are known:

$$\frac{[H^+]\,[H_2X^-]}{[H_3X]} = K_1 \tag{1}$$

$$A = \frac{[H_3X]}{[H_2X^-]} = \frac{[H^+]}{K_1} \tag{2}$$

$$\log \frac{[H_3X]}{[H_2X^-]} = pK_1 - p\mathrm{H} \tag{3}$$

$$\frac{[H^+]\,[HX^=]}{[H_2X^-]} = K_2 \tag{4}$$

$$B = \frac{[HX^=]}{[H_2X^-]} = \frac{K_2}{[H^+]} \tag{5}$$

$$\log \frac{[HX^=]}{[H_2X^-]} = p\mathrm{H} - pK_2 \tag{6}$$

$$\frac{[H^+]\,[X^{\equiv}]}{[HX^=]} = K_3 \tag{7}$$

$$[HX^{2}] = K_2 \frac{[H_2X^-]}{[H^+]} \tag{8}$$

$$C = \frac{[X]}{[H_2X^-]} = \frac{K_2K_3}{[H^+]^2} \tag{9}$$

$$\log \frac{[X^{\equiv}]}{[H_2X^-]} = 2\,p\mathrm{H} - pK_2 - pK_3 \tag{10}$$

Inasmuch as equations (3), (6), and (10) involve a linear relationship between the logarithm of the ratios and pH, only two points need be calculated for the graphical representation of the variation of each ratio with pH. Regular coordinate paper may be used.

In use, log A, log B, and log C may be read directly from the graph for any desired pH value covered by the plot, and values of A, B, and C thereby obtained. Since the ratios A, B, and C have, as their common denominator $[H_2X^-]$, one may write:

$$[H_3X] : [H_2X^-] : [HX^{2-}] : [X^{3-}] = A : 1 : B : C \tag{11}$$

and the fraction of "total X" in a particular species is given by:

$$\frac{[H_3X]}{\text{"total X"}} = \frac{A}{A + 1 + B + C} \tag{12}$$

$$\frac{[H_2X^-]}{\text{"total X"}} = \frac{1}{A + 1 + B + C} \tag{13}$$

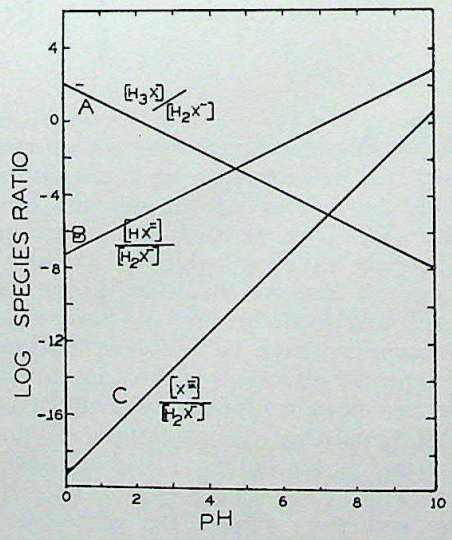
$$\frac{[HX^=]}{\text{"total X"}} = \frac{B}{A + 1 + B + C} \tag{14}$$

$$\frac{[X^{\equiv}]}{\text{"total X"}} = \frac{C}{A + 1 + B + C} \tag{15}$$

While the graphical treatment and evaluation is not recommended for isolated computations where only a few values are to be obtained, it is of great value when a more thorough study of a system is to be made.

For a weak dibasic acid, the system involves one less equilibrium expression and computations are correspondingly simpler; for weak monobasic acids the Henderson-Hasselbalch relationship may be used to advantage.

The figure shows a typical graph for a tribasic acid, phosphoric acid being used as an example.



Variation of log species ratio with pH for phosphoric acid. Dissociation constants: $K_1 = 7.5 \times 10^{-3}$, $K_2 = 6.2 \times 10^{-8}$, $K_3 = 4.8 \times 10^{-13}$.

[1] Though only the ionization of polybasic acids is treated here, the fundamental phenomenon is also applicable to other equivalent reactions such as cation hydrolysis and complex ion formation reactions which are pH dependent and take place step-wise.

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Formation of Monothiocyanatoiron(III)

A photometric equilibrium study

No approach to the analysis of a homogeneous equilibrium system is more illuminating than the method of simple spectrophotometry. Any student can immediately and intuitively appreciate the necessity of a relationship between color intensity and concentration; the useful quantitative relationships (Beer's law) are easy to teach; the apparatus (e.g., Leitz-Ruoy filter photometer) can be beautifully simple and yet have quite pleasing accuracy; and very important at an early stage of instruction, the equilibrium system can be thoroughly examined without disturbing it or destroying a sample. For these reasons the author feels that beginning equilibrium experiments using photometry are especially instructive.

The "blood-red" complexes of thiocyanate with iron(III) are well known in qualitative analysis, quantitative determination of iron, and considerable research literature has accumulated on the formation and nature of the series of species involved. At least one recent general chemistry laboratory manual (*1*) shows a simple visual colorimetric experiment designed to obtain an approximate value for the formation quotient of the first complex ion, monothiocyanatoiron(III). It was felt that although this experiment was instructive as published, it was inherently less accurate than desired, suffered from an assumption that one can reliably prepare a solution of known concentration of the single complex, and could be strikingly improved if redesigned with a procedure involving simple photometric measurements. The discussion and directions given to the students are an adaptation of the work by Frank and Oswalt (*2*), and the reader is referred to their paper for a fuller discussion.

Definition of the Chemical System. Thiocyanate ion can react with ferric ion in acid solution to form a series of thiocyanato- complexes:

$$Fe^{+++} \rightleftharpoons FeSCN^{++} \rightleftharpoons Fe(SCN)_2^{+} \ldots \text{etc.}$$

In the presence of high concentrations of thiocyanate the higher complexes predominate, but if the molarity of thiocyanate is very low the only complex formed in appreciable amount is the monothiocyanatoiron(III) ion, according to:

$$Fe^{+++} + SCN^{-} \rightleftharpoons FeSCN^{++} \qquad (1)$$

with the equilibrium quotient:

$$Q = \frac{[FeSCN^{++}]}{[Fe^{+++}][SCN^{-}]} \qquad (2)$$

In this experiment the concentration of thiocyanate ion will always be less than 0.0002 M, and since the equilibrium quotient for the formation of the *di*thiocyanato complex is approximately 13 (*3*), then the ratio:

$$\frac{[Fe(SCN)_2^{+}]}{[FeSCN^{++}]} = 13[SCN^{-}] = 0.0026 \textit{ maximum}$$

Therefore, the higher complex will never be more than about a quarter of a per cent of the total.

Another possible chemical complication which must be avoided is the formation of hydroxyiron(III) species. The aquo-ferric ion is a moderately strong Brønsted acid, with a dissociation quotient (ionic strength = 0.5) of about 6×10^{-3} (*4*). Therefore, if the concentration of monohydroxyiron(III) ion is to be reduced to negligible values, the hydronium ion concentration should be of the order of 0.5M. In this experiment this will be achieved by using such a concentration of perchloric (or nitric) acid.

At this acidity, the uncomplexed iron(III) ions do not absorb visible light appreciably, and so the thiocyanate complex is the only colored species. It is assumed that thiocyanate does not take on protons (i.e., that thiocyanic acid is strong), but this is a point which is not clearly settled in the literature. Students might be asked to discuss the quantitative implications of this uncertainty.

The procedure will be to add small successive portions of a solution containing 0.1 M iron(III) ion and 0.5 M hydronium ion to a known volume of a solution containing 0.0002 M thiocyanate ion and 0.5 M hydronium ion. Thus, both the ionic strength and the acidity will remain effectively constant during the experiment. Either a nitrate or a perchlorate medium must be used because other anions form iron complexes. If nitric acid is used it would be wise to use fresh "white" concentrated acid to make the solutions and avoid the possibility of oxidation of thiocyanate by oxides of nitrogen. Or better, the nitric acid can be cleaned effectively by adding a few crystals of sulfamic acid (*5*), which will not interfere with the experiment.

With each addition of the iron(III) solution, the concentration of the monothiocyanate ion will increase, and the transmission or absorbance, A, of the solution can be measured. Since the complex is the only absorbing species,

$$A = ab[FeSCN^{++}] \qquad (3)$$

where a is the absorptivity and b is the cell length. However, the absorptivity cannot be determined in the usual way because it is not possible to prepare a solution with a known concentration of complex (unless one knows the precise value of the equilibrium quotient, which would make this experiment pointless). It is not feasible to add enough iron(III) ion to force the reaction quantitatively to the right, converting the known total amount of thiocyanate completely to the

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colored complex. This is contrary to the assumption involved in the simple visual experiment referred to earlier. For accurate results it is necessary to introduce a mathematical interpretation of the data which does not require knowledge of the absorptivity. This can be done as follows:

Algebraic Principles. For any of the equilibrium mixtures involved in this experiment, the total molarity of thiocyanate, C_s, and of iron, C_f can be represented by:

$$C_s = [SCN^-] + [FeSCN^{++}] \quad (4)$$

$$C_f = [Fe^{+++}] + [FeSCN^{++}] \quad (5)$$

Equations (2)–(5) may be combined to give:

$$Q = \frac{A/ab}{(C_f - A/ab)(C_s - A/ab)} \quad (6)$$

Now, C_f and C_s at any point can be calculated by ordinary molarity-volume relationships. The absorbance can be measured in the usual way. But for a direct solution of the equation to find Q it would be necessary to know the product ab and this information is not directly available. However, equation (6) is a regular quadratic expression in terms of the concentration of complex, i.e., A/ab, and Frank and Oswalt showed that it was convenient to use a series approximation formula (*6*) for solution:

$$A/ab = \frac{C_f C_s}{C_f + C_s + 1/Q} + \frac{(C_f C_s)^2}{(C_f + C_s + 1/Q)^3} + \ldots \quad (7)$$

because at the low concentrations of iron and thiocyanate used in this experiment the first term alone on the right side accounts for better than 99% of the value of A/ab. Therefore, neglecting the higher terms of the series, equation (7) can be rearranged to give:

$$\frac{C_f C_s}{A} = \frac{1}{abQ} + \frac{(C_f + C_s)}{ab} \quad (8)$$

which is the form used by Frank and Oswalt. When values of $C_f C_s/A$ are plotted versus corresponding values of $(C_f + C_s)$ a straight line should be obtained with a slope/intercept ratio equal to the value of the equilibrium quotient, Q.

An alternative arrangement of the equation is as follows:

$$\frac{A}{C_f C_s} = abQ - \frac{A(C_f + C_s)Q}{C_f C_s}$$

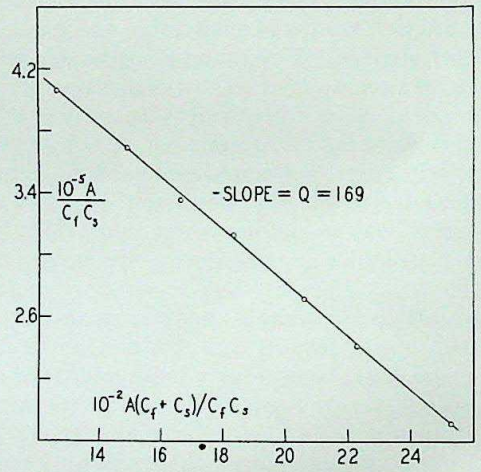
and a plot of $A/C_f C_s$ versus $A(C_f + C_s)/C_f C_s$ should be linear with the slope equal to $-Q$. Thus, it turns out to be unnecessary to know the absorptivity of the complex ion, although this quantity can be calculated as a byproduct in the determination of Q.

Laboratory Directions. Prepare the dilute thiocyanate solution as follows: into a 100-ml. volumetric flask pipet 10 ml of the provided 0.002 *M* (note the precise molarity given by the instructor) potassium thiocyanate, and also pipet 25 ml of 2.0 *M* perchloric (or nitric) acid. Dilute to the mark, mix well, and pour "quantitatively" into a 250-ml beaker. It will be assumed that the flask *delivered* 100.0 ml.

Use a 1-ml pipet to add successive portions of the provided 0.1 *M* (note the precise molarity according to standardization) iron(III) perchlorate (or nitrate) solution which also contains 0.50 *M* acid. After each addition, stir thoroughly, pour into a photometer cell, measure the absorbance at the wavelength of maximum absorption (445–450 mμ), and *return* the sample to the beaker, being careful to avoid loss of solution. The number of points to be taken is arbitrary, from five to ten.

Calculations. The values of C_f and C_s at each point are calculated simply by considering the dilutions which the solutions have undergone. The values of absorbance, which may have to be calculated from per cent transmission readings, are not corrected for dilution. Make the plot(s) as indicated, taking special care to draw the best straight line. The method of least squares is recommended but is not necessary. Calculate the value of Q, and write a brief discussion of the errors which are inherent in the experiment as it has been carried out.

Results. The figure shows the experimental results of one of the sophomore students. It is typical that the data fall on a good straight line, but because of miscalculations, carelessness in plotting, graphs which are too crude, etc., there will usually be a considerable spread in values of Q. The accepted literature value for Q is 138 at 25°C (*2*,*7*). We have obtained values about 20% higher on the average, probably due to color fading resulting from exposure to light. It would be best to dim the room and to work quickly.



Graphical determination of the formation quotient. Data of Oren Anderson, Carleton College.

This experiment seems to be a very good one because it brings out so many important principles of quantitative work: the use of volumetric ware, molarity-volume relationships, spectrophotometry, the setting up of a mathematical model for a proposed chemical system, the problem of using extrapolation when there are too many unknowns, the satisfaction of using one's own data in the interpretation, the comparison with literature values, and the criticism of the experiment as a whole.

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A Modular Approach to Chemical Instrumentation

Modern complex instruments are becoming common tools of the professional chemist, and the problem of educating future chemists to use these tools intelligently is beginning to receive serious attention. An attempt to simplify the problem by regarding instruments as "black boxes," whose internal operations are of no concern to the chemist using them, has resulted in costly errors and wasted effort. Instruments are used without proper regard for their operational characteristics and limitations. A common complaint of industrial supervisors and research directors is that the recent graduate usually believes that almost any problem can be solved quickly and easily by the purchase and application of some instrument (usually an expensive one) and that problems presented by limitations of the principle employed by the instrument become apparent to him only after he has had experience with its application.

The problem of properly preparing future chemists to make the best use of contemporary instruments, and of instruments yet to be developed, may be more soundly approached by helping the student to acquire a sufficient knowledge of the principles of chemical instrumentation and their application, so that he has an intuitive sense in the use of an instrument. Instrumental principles are fairly easy to present in lectures and in texts, but familiarity with the application of these principles is not so easy for the student to obtain. The modern instruments which apply the principles are designed for precise, trouble-free operation, which usually means that they are enclosed, and sometimes sealed, to prevent the entrance of dust or light. The more complex the instruments, the less likely will they be open to inspection that will reveal their operation.

To assist the student to acquire familiarity with the application of instrumental principles, a modular approach is taken. The student is provided with relatively simple instrument building blocks, or modules, each of which may be studied in detail to observe the application of a principle of chemical instrumentation, and which may subsequently be interconnected to form operating instruments. The student progresses from the relatively simple to the very complex by the interconnection of appropriate modules.

The principle considerations which have influenced the design of the modules are (1) simplicity of construction (including the use of commercially available hardware), (2) accessibility of all parts to inspection, (3) interchangeability of all modules having similar functions, (4) low cost, and (5) ruggedness to withstand student handling, inspection, and operation. Each module is sufficiently simple to permit its construction on a limited budget.

The set of basic modules is listed in Table 1. Additional modules for more complex automatic and recording instrumentation are being tested, and will be described in a later publication. The modules included in this paper have been used by students participating in the development program for two years and in formal laboratory instruction for one year. Detailed photographs of the modules have been taken, and dimensions have been drawn on the photographs so that they may be duplicated by students or instructors. Publication of a construction manual, including the dimensioned photographs, is now being undertaken.

Figure 1 is a dimensioned photograph of a light source (Module 3) with its side open. When in use, a metal side-plate held by four spring clips closes the side. Other views of this module have been prepared with the remaining dimensions necessary to facilitate its

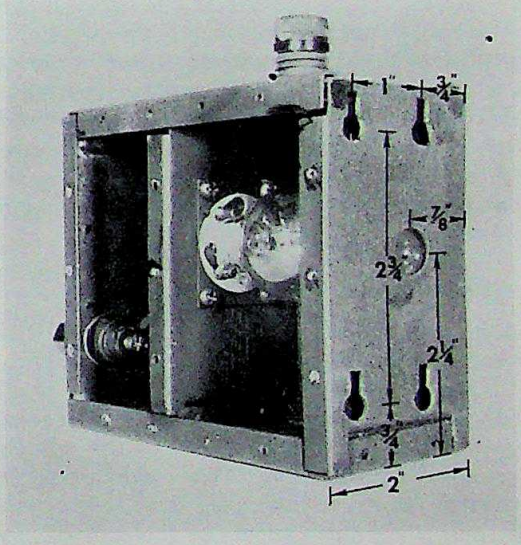


Figure 1. Module 3 (light source).

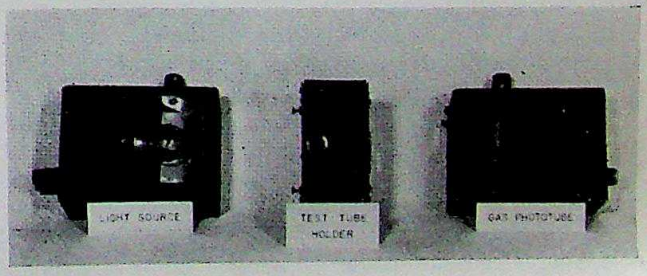


Figure 2. Modules 3, 6, and 15.

This work has been supported by a grant from the National Science Foundation.

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Table 1. Instrumentation Modules

1. Photovoltaic cell housing—with shutter
2. Microammeter—100 μa, 1 ma, 10 ma ranges, overload-protected
3. Light source—produces focused beam
4. Light source supply transformer
5. Constant voltage light source supply transformer
6. Test tube holder—with filter holder
7. Beaker holder—with filter holder and interchangeable lids (one with a light-shield for photometric titrations)
8. Beam splitter—prism or semi-silvered mirror
9. Test tube holder, right angle—with filter holders
10. Beaker holder, right angle—with filter holders and interchangeable lids as in module 7
11. Grating monochromator—with adjustable entrance and exit slits and wavelength selector
12. Prism monochromator—with adjustable entrance and exit slits and wavelength selector
13. Interference-filter wedge monochromator—with adjustable entrance and exit slits and wavelength selector
14. Vacuum phototube housing—with shutter
15. Gas phototube housing—with shutter
16. Resistance photocell housing—with shutter
17. High-impedance amplifier—input ± 1.5 V.D.C. at 10^9 ohms, output ± 1.5 V.D.C. at 1500 ohms (or ±1 ma)
18. Current amplifier—input 0.1, 1, 10, and 100 μa, 1 ma, output 1 volt at 1000 ohms (or 1 ma)
19. Regulated power supply—output of +150 V.D.C., +105 V.D.C., −150 V.D.C. at 20 ma (all regulated), and 6.3 V.A.C. unregulated
20. Variable power supply—output of 0 to 250 V.D.C. at 125 ma and 6.3 V.A.C.
21. Photomultiplier tube housing—with shutter
22. Photomultiplier power supply
23. Aspirator burner—with focusing lens and mirror, and filter holder
24. Magnetic stirrer
25. Ultraviolet source—mercury vapor lamp and power supply

construction. Figure 2 shows side views of a light source and a gas phototube receptor, and a top view of a test tube holder. The bracket at the right in the test tube holder is the holder for 2-in. square filters.

Only a few of the experiments that may be performed by students using these modules will be discussed with the realization that instructors will vary in their emphasis of functional principles and will use the modules to illustrate their presentation. A manual of experiments performed by our students is in preparation for publication.

Optical Experiments

Modules 1 and 2 may be connected to form a simple photoelectric photometer. This will introduce the student to the self-generating barrier-layer photocell, and the instrument may be used with a meter stick and a 40 watt incandescent bulb to verify the relationship of distance to light intensity. The student will observe non-linearity at high intensity levels, due to the transit time of current-carriers in the semi-conducting layer, and a background current at low intensity, due to room illumination. He may then proceed to the use of modules 14, 18, 19, and 20 which, with module 2, will form a photometer having a wider range of linearity. Module 19 supplies power to module 18, and module 20 supplies a variable potential to module 14.

Modules 3 and 6 may then be connected to each other and to module 1, by their simple keyway connectors, to form, with module 2, a simple photoelectric absorption instrument, with power supplied by either module 4 or 5, which may be used for practical turbidimetry or colorimetry measurements. Figure 3 shows a student inserting a sample tube in the colorimeter which he has assembled from modules 4, 3, 6, 1, and 2 (reading from left to right). The principle function of this instrument is to illustrate instrumental principles such as the importance in absorptimetry of having a source of constant radiant flux, and of the spectral response of the receptor. The effectiveness of a constant-voltage light source supply transformer is checked by first connecting a variable-voltage transformer (Variac or Powerstat) between the 115 volt source and the unregulated light source supply transformer (module 4) and taking a series of photocurrent readings at various settings of the Variac, then replacing module 4 by module 5 and repeating the same measurements. The linearity of the receptor is easily checked by using a series of Kodak Wratten neutral density filters in the filter holder of module 6. The spectral response of the source-receptor combination may be checked by the use of a set of calibrated interference filters, if these are available, or this experiment may be performed later with the grating monochromator after calibration.

An alternative method of compensating for changes in the source flux, and a method for directly observing the ratio of absorbance of two samples, is to split the source flux into two beams and use the output of a second receptor as a reference. This may be accomplished by placing module 8 between modules 3 and 6 of the previously described colorimeter, and then connecting another receptor, either directly or through another module 6, to the right angle exit port of module 8. The outputs of the two receptors are compared with a simple bridge circuit, and their ratio is the input to module 18. We use two identical receptors to correspond to practical commercial instrumentation, but unlike receptors may be used within their linear response regions if the expense of duplicating receptors is a factor. The limitations of compensation by ratio comparison will become evident to the student during the experiment.

The grating monochromator, module 11, is completely open to inspection by the student. After interconnecting modules 3, 5, and 11, the student may trace the beam, using a small strip of white paper, from the small right-angle mirror through the entrance slit from which it goes to the collimating mirror as a diverging beam of decreasing intensity, from the collimating mirror toward the grating as a parallel beam of constant intensity, from the grating as dispersed radiation, and from the collimating mirror to a focused spectrum at the slit. Figure 4 shows two students experimenting with the grating monochromator. The student on the left is adjusting the position of the collimating mirror, while the student on the right is controlling the position of the grating with his left hand to

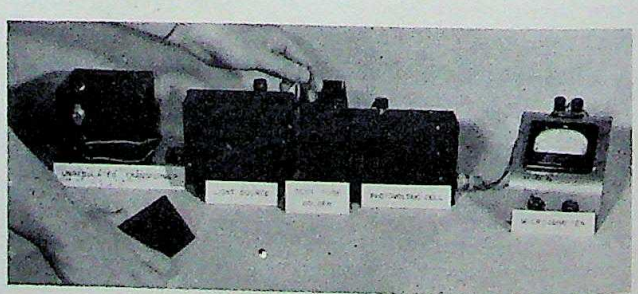


Figure 3. Colorimeter assembled from modules.

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present a desired portion of the spectrum exit slit while tracing the rays with the small strip of white paper in his right hand.

Modules 2, 6, 14, 18, 19, and 20 may be attached to form a complete grating spectrophotometer. The monochromator is wavelength-calibrated by replacing modules 3 and 5 by module 25 and using the mercury lines of that source. The calibrated monochromator is then ready for numerous experiments, including plotting the transmission curve of a Wratten filter and

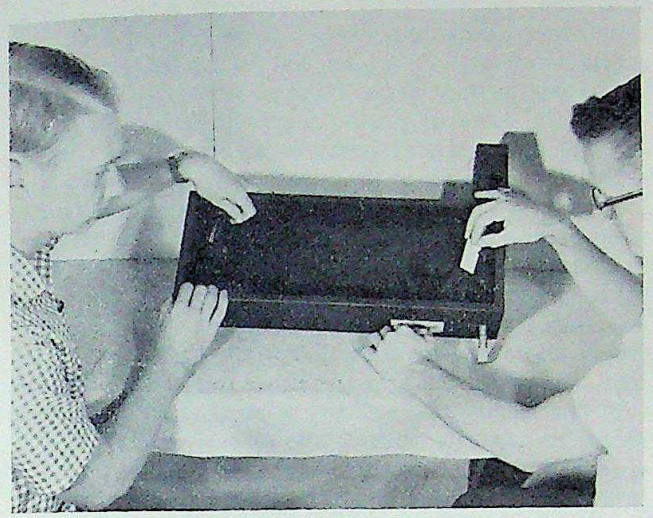


Figure 4. Adjusting the grating monochrometer.

the determination of the spectral sensitivity and linearity of various receptors. At this point the student may question the linearity of the amplifier. He is then provided with a decade resistance box and a mercury reference battery, with which he can accurately determine its linearity and input resistance.

Other Experiments

Module 23 (aspirator burner) may be used with other modules to assemble a flame photometer, with internal standard operation if desired. Figure 5 shows students preparing to study flame photometry. The student at the left is filling the aspirator with the solution to be studied. Light from the flame will pass through a filter in module 6, and be received by module 14 (vacuum phototube). The student on the right is completing the electrical connections between modules 2, 18, 19, and 20 to measure the photocurrent produced.

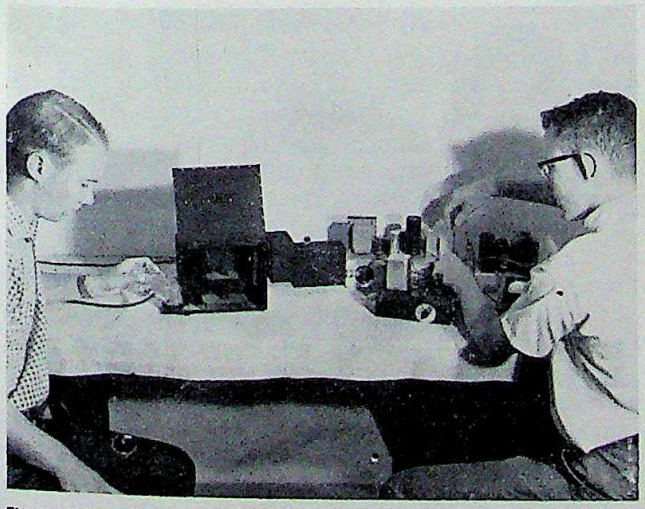


Figure 5. Assembling a flame photometer.

The interconnection of module 17 with modules 2 and 19 forms an electrometric instrument which may be used to determine *p*H with student-constructed calomel and quinhydrone electrodes, or with a commercial glass indicator electrode and either the student-constructed or a commercial calomel electrode.

When module 24 is used with module 7, titrations may be performed with the endpoint (colorimetric, spectrophotometric, nephelometric, turbidimetric, or fluorimetric) detected photometrically, or with an electrometric endpoint (*p*H, potentiometric, redox, or amperometric) by using the appropriate additional modules. Coulometric titrations and polarography are other electromatic methods that can be studied using these modules. Table 2 is a list of instruments which may be assembled from these modules.

It should be noted that our students become acquainted with electrical measurements, and power supply, dc amplifier and ac amplifier circuitry during the first third of the semester. We have used the excellent electronics chapter in "Experiments for Instrumental Methods" by Reilley and Sawyer as a text, and electronic modules derived from that text. The last two-thirds of the semester are devoted to experiments with instruments constructed from the modules described in this paper.

Student response and achievement have been excellent, and we believe that the use of the modules has helped them achieve understanding of the instrumentation principles which will permit them to use complex instruments of the present and future with confidence and success.

The assistance of several undergraduate students in the design and construction of these modules is gratefully acknowledged, with special credit to David Ash for his many significant contributions to the project.

Table 2. Instruments Which May Be Assembled From the Modules

I. Simple photoelectric photometer—modules 1 and 2
II. General purpose photoelectric photometer—modules 2 (14, 15, or 16), 18, 19, and 20
III. High sensitivity photoelectric photometer—modules 2, 21, and 22
IV. Turbidimeter—modules 3, (4 or 5), (6 or 7), and instrument (I or II)
V. Nephelometer—modules 3, (4 or 5), (9 or 10), and instrument (II or III)
VI. Colorimeter—modules 3, (4 or 5), (6 or 7), and instrument (I, II, or III)
VII. Compensating turbidimeter, nephelometer, or colorimeter—module 8 and appropriate instrument (IV, V, or VI) with an additional module (14, 15 or 16)
VIII. Spectrophotometer—modules 3, (4 or 5), (6 or 7), (11, 12, or 13), and instrument (II or III)
IX. Fluorometer—modules (9 or 10), 25, and instrument (II or III).
X. Flame photometer—module 23 and instrument (I, II, or III)
XI. Internal—standard flame photometer—modules 8, 23, and instrument (I or II) with an additional module (14, 15, or 16)
XII. Flame spectrophotometer—modules (11, 12, or 13), 23, and instrument (II or III)
XIII. Turbidimetric, nephelometric, colorimetric, spectrophotometric, or fluorometric titrator—module 24 and appropriate instrument (IV, V, VI, VII, VIII, or IX)
XIV. Electrometric titrator (redox or *p*H)—modules 2, 17, 19, and 24
XV. Coulometric titrator—module 20 and instrument (XIII or XIV)
XVI. Manual polarograph—modules 2, 18, 19, and 20

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Collected by
Alfred B. Garrett
Ohio State University
Columbus

The Flash of Genius, 13

Carbon-14 Dating: Willard F. Libby

Often interesting and extremely significant applications develop from fundamental research. This is the case of the method of dating geological time periods and archaeological objects with the long-lived radioisotope of carbon, carbon-14 (half-life 5760 years), and other long-lived isotopes. W. F. Libby, the American scientist who developed this process in the late 1940's, describes his work as follows.[1,2]

"The radiocarbon dating technique was discovered as a result of a general interest in the possible effects of cosmic radiation on the earth and its atmosphere. It became apparent, as a result of thinking about the possible effects of high energy protons which, of course, constitute the main part of the cosmic rays, that in the bombardment of oxygen and nitrogen nuclei that ^{14}C should be the most abundant product in the conversion of any neutrons produced in the initial high energy collisions because neutrons released in the atmosphere will always form ^{14}C in the main.[3]

"The realization of this fact, and learning of the observations by Dr. Korff of New York University of neutrons as cosmic ray secondary products, led to radiocarbon dating via the following chain:[3,4]

"Radiocarbon atoms introduced into the atmosphere make radioactive carbon dioxide.

"Radioactive carbon dioxide thus produced in the atmosphere will mix with normal carbon dioxide making the mixture radioactive.

"Since plants live off carbon dioxide and depend on it for carbon, this makes all plants on earth radioactive.

"Since animals live off plants, this makes all animals radioactive.

"Since the turnover time for the biosphere is short compared to the half-life of ^{14}C (5760 years), the specific radioactivity of all living matter should be the same and should be proportional to the ratio of the neutron production rate per unit area of the earth's surface to the total amount of carbon in equilibrium with atmospheric carbon dioxide per unit area of surface. In calculating this ratio, one must take account of the ocean. It turns out that the ocean contains the major part of the carbon exchanging with the atmosphere and fortunately the ocean carbon content can be estimated quite accurately. Although the carbon content of the biosphere is difficult to estimate, the total of the biosphere plus the carbonate and bicarbonate in the sea can be estimated quite accurately.

"If the cosmic-ray intensity has remained constant with time, neglecting any fluctuations occurring in a time short compared to the mean life of ^{14}C, the specific radioactivity of ancient living matter should have been the same as for living matter today.

"At the time of death, the assimilation of radiocarbon stops abruptly because the only contact living organisms have with the atmosphere is through the life process. Exchange reactions between organic molecules and atmospheric carbon dioxide are too slow to be important and rotting and decay processes lead to reduced molecular weights, so that all one has to do is to select material in which the smaller molecules formed in the decay process can be washed out to be sure that primeval carbon is being measured. In this way, the specific radioactivity of ancient material gives its age at the rate of 50% loss of activity every 5760 years elapsed since death.

"Since the rate of ^{14}C decay is unaffected by any known physical conditions we could expect that this would give an absolute time or age. Of course, we know that differences between species, small inconstancies in the average cosmic ray flux and errors in measurement can all add up to give error in the final dates. But, in principle, the method should produce absolute dates if the assumptions given are correct.

"The method can be applied to samples of known age back through the dawn of history, 5,000 years ago.

"Out of these thoughts, we proceeded to look for radiocarbon in nature and after having found it, developed a method for measurement which would be satisfactory and then proceeded to check against samples of known age back to about 5,000 years and applied to prehistoric materials. The results seem to be satisfactory and it does appear that the technique is sound for the last 5,000 years, and probably as far back as radiocarbon can be measured—about 40,000 or 50,000 years."

"The research on radiocarbon dating was carried out in several stages. In the first place, my collaborator, E. C. Anderson and I had to determine whether the living material actually had the radioactivity expected. At that time we had no measurement techniques sufficiently sensitive to detect the radioactivities involved directly because these levels are quite low. Later we developed methods for making the measurement but at that time we did not have them, so we used the method of concentrating the heavy isotope of carbon. An apparatus for this purpose had been built by and was being used by A. V. Grosse of Temple University, then of the Houdry Process Corporation at Marcus Hook, Pennsylvania. Grosse was concentrating the carbon-13 isotope for medical tracer purposes and kindly agreed to try to concentrate some biological methane for the test so crucial to our research. We had to use biological, as contrasted with

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[1] Personal Communication.
[2] Libby, W. F., *Science*, Vol. 133, March 3, pp. 621–9 (1961).
[3] Libby, W. F., *Phys. Review*, 69, 671 (1946).
[4] Anderson, E. C., and Libby, W. F., *Phys. Rev.*, 72, 931 (1947).

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petroleum, methane, for we had at this point arrived at a distinction between living and dead organic chemicals. We had both "dead" methane and "living" methane in the sense that methane from oil wells in which the oil has been long buried would be expected to be entirely free from radiocarbon while the methane made from the disintegration of living organic matter should contain radiocarbon with an activity of 14 disintegrations per minute per gram of carbon.[5] The task was to take this living methane and concentrate it in the isotope separation column to see whether the heavily enriched product was radioactive. Happily for our research, it was found to be so, and to about the expected degree. The material used was methane gas from the sewage disposal plant of the city of Baltimore."[2]

[5] Anderson, E. C., and Libby, W. F., *Science*, 105, 576 (1947).

Robert Vollmer
Case Institute of Technology
Cleveland, Ohio

Beam Protective Device for an Automatic Analytical Balance

The knife edge of an analytical balance can be damaged if the user forgets to arrest the beam before changing the beam loading. Damage of this sort can be greatly lessened by a device which emits an audible signal if the balance door is raised with the beam in an unarrested position. We have been successfully using a warning device of this kind on the automatic balances in both our general chemistry and analytical chemistry laboratories.

Such a device can be installed on a balance in about 2 hrs. at a parts cost of about four dollars. Figures 1 and 2 show the general installation and wiring diagram for installing the audio-device on an Oertling balance, Model HO5. The procedure is as follows:

Remove the left side panel, held by six self-tapping screws, for drilling and mounting of the parts. Mount the buzzer on the inside and the buzzer microswitch on the outside of the panel. The switch is positioned so that when the sliding door is closed its left protruding edge compresses the microswitch bar opening the circuit.

Wire the buzzer and switch in series. Then run the two wires along the top and down the back of the panel. An interlock switch or a 2 ft length of cord will facilitate the removal of the case for easy servicing.

Run one of the wires over to the light bulb. Pinch the wire under the light bulb flange; or if preferred, solder the wire to the copper strip which connects to the bulb ring contact.

Run the other wire to the balance microswitch. Connect to one of the wired terminals on the switch. If the buzzer operates with the beam arrested, remove the wire and connect to the other wired terminal on balance microswitch.

By means of a pair of diagonal pliers, twist the panel slightly, at point 1 on Figure 1, in order to eliminate any side play of the panel and to guarantee proper actuation of the buzzer microswitch.

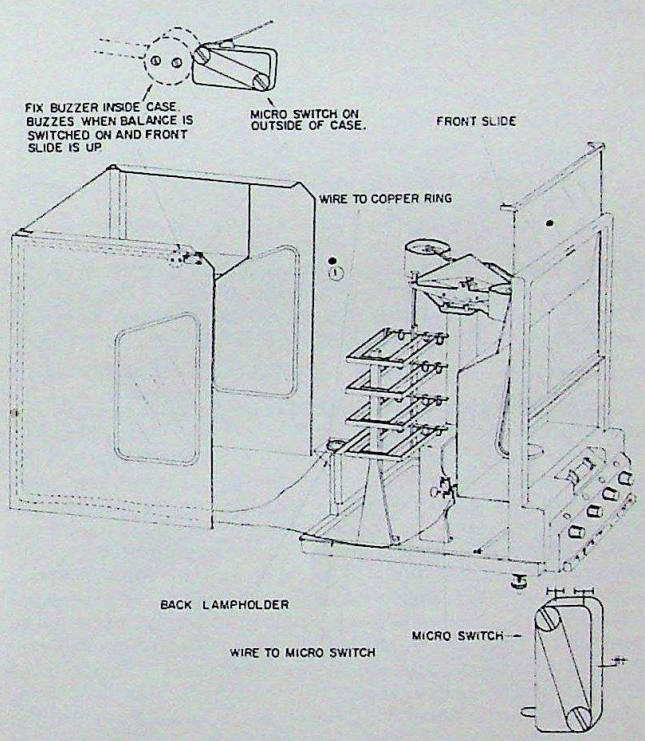


Figure 1.

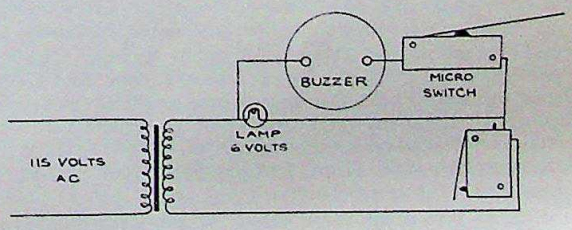


Figure 2.

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James M. Gaidis
Contributed by
Eugene G. Rochow
Harvard College
Cambridge, Massachusetts

The Catalyzed Decomposition of Potassium Chlorate

Since the turn of the century, fewer than a half-dozen articles have been published on the thermal decomposition of chlorates or perchlorates, and there have been none since Tian and Svilarich (*1*) examined the catalyzed decomposition of perchlorates in 1930.[1] Otto and Fry (*2*, *3*) first showed that the thermal decomposition of potassium perchlorate catalyzed by Fe_2O_3 was unimolecular. A year later, they found that the non-catalyzed decomposition of potassium chlorate also was unimolecular (at least approximately), when decomposing thus:

$$2KClO_3 \rightarrow 2\ KCl + 3O_2$$

To adjust for the disproportionation

$$4KClO_3 \rightarrow 3KClO_4 + KCl$$

and the concomitant decomposition

$$KClO_4 \rightarrow KCl + 2O_2$$

they introduced elaborate corrections, but in half of their trials, these last two reactions consumed 85% of the original chlorate, leaving only a small fraction to undergo the reaction as first written. The most elaborate corrections could hardly be expected to remove all the error involved.

In 1820 Döbereiner first used manganese dioxide as a catalyst for the chlorate decomposition, and shortly afterward it was realized that its use was accompanied by the evolution of minute quantities of a strongly-oxidizing gas along with the oxygen. Oxides more acidic than manganese dioxide gave larger quantities of the strongly-oxidizing gas. In 1855 C. F. Schönbein claimed that the gas is ozone, as did Brunk (*4*) in 1893, but Leeds (*5*), McLeod (*6*), and Sodeau (*7*) all have claimed that the gas is chlorine.

The present study was undertaken because the author had not found in his textbooks any adequate explanation of how or why manganese dioxide acts as a catalyst in the decomposition of potassium chlorate. Moreover, almost everyone who has used the reaction has ignored the presence and the nature of the strongly-oxidizing gas. In view of the uses to which oxygen from potassium chlorate is put, such an impurity would not be negligible.

Most previous workers have used 10 to 20% of catalyst, but preliminary experiments in the present work showed considerable advantage in using only 0.2% of MnO_2. With this limited amount of catalyst the temperature may be increased enough to fuse the potassium chlorate, resulting in a homogeneous

[1] After this paper was submitted, a note on the nature of the perchlorate decomposition was submitted by O. Bostrup, K. Demandt, and K. O. Hansen as one of the Textbook Errors of This Journal and appeared 39, 573 (1962).

Contributor's Note: It is a time-honored custom in many colleges to allow undergraduates of marked research ability to pursue their own interests quite outside of (and in addition to) the regular course curriculum. Traditionally, some professor spots a student of exceptional ability and encourages him by providing laboratory space, supervision, tutelage, unlimited discussion, access to books, or whatever else the student needs to develop his scholarly bent. Sometimes an able student who is too quiet or self-effacing to make any claim to such personal attention, or even to be noticed, will simply find it impossible to keep away from the graduate research laboratories, and will eventually be taken in as an informal apprentice. This is in the tradition of the ancient European university, a tradition transplanted to our country long ago. Many of our outstanding chemists went through such an experience, and for them it made all the difference between remaining an ordinary student and becoming an exceptionally inquisitive scholar.

By its very nature, such encouragement of undergraduate research (especially among freshmen and sophomores) cannot be organized or evaluated on a competitive basis. It remains a personal relationship which depends upon personal interests and personal characteristics; it has nothing to do with credits or with coverage of a subject. Nevertheless, it does take a great deal of a professor's time (no matter how gladly given), and it does compete with all the worthy courses in the student's schedule. As today's curricula become more crowded, there is danger that such independent and informal study might be squeezed out, to the great loss of future scholarship.

In order to encourage the practice of early individual study without interfering with its personal and informal nature, the faculty of Harvard College began three years ago to grant up to one-fourth of the first-year's credit for "ungraded independent study." The practice has been limited to those students who, in the opinion of the Office of Advanced Standing *and* a professor who has agreed to direct the work, would advance faster toward intellectual maturity in this way than by staying within the regular course framework. The permission does not carry with it waiver of any required courses or subjects; it simply moves a research elective down into the freshman (and inevitably the sophomore) year for those who are well enough prepared or sufficiently gifted to benefit from it. As for the "independent study," it continues to take whatever form the professor deems best, the forms being as varied as are people and subjects.

The following paper is condensed from one of the many freshman and sophomore research reports I have received during the past three years, most of which, I believe, contain significant research results. This particular report is presented (1) as an example of what can come out of underclass research, quite apart from any benefit to the student, and (2) because the subject is of interest to many teachers of secondary-school and college chemistry. It represents part of two year's work on the part of Mr. Gaidis, for which he received one semester-course credit under the program. The project was not assigned, but (as usual) was the student's own choice. *All* the equipment was designed and built by Mr. Gaidis, and he alone drew the conclusions, wrote the paper, and drew the diagrams. I have rearranged the order, the references, and the diagrams to comply with the editorial practices of This Journal, but have not altered his thoughts.

Eugene G. Rochow

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colored liquid, yet without causing an excessive rate of oxygen evolution. Liquid-phase reactions, of course, offer the advantage of greater reproducibility in kinetic measurements. Some conclusions could also be drawn from the color of the liquid. (Only four writers previously have described a purple melt, for example. For the rest the color was hidden, undoubtedly by an excessive amount of catalyst.) Kinetic measurements were made at different temperatures, and the evolved gases were examined.

Experiments Performed

The apparatus was not complicated. Known mixtures of $KClO_3$, $KClO_4$, and catalyst were placed in test tubes, and the gases evolved from these reaction vessels forced water from flasks into 500-ml graduates which indicated 25-ml intervals for timing and for rate calculations (Fig. 1). The furnace, designed to heat five test tubes simultaneously, was of brass and asbestos, wound with a nichrome resistance element.

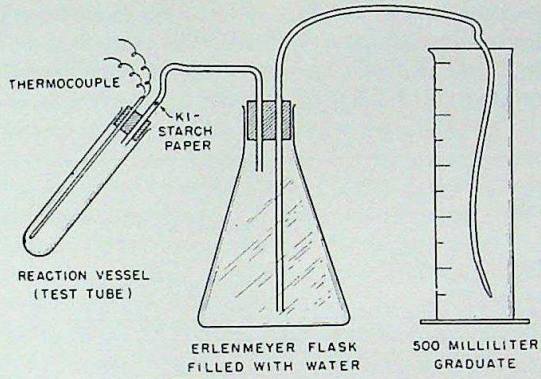


Figure 1. Gas collection apparatus.

Two and one-half kilograms of brass in the furnace provided a large thermal inertia, keeping temperature variations to a minimum. An old Brown potentiometer, adapted by means of a stepping relay to accept six inputs in rotation (one for each of the five reaction tubes and one for the brass block), recorded the temperature of a protected chromel-alumel thermocouple immersed in the molten reactants (Fig. 2). Close-fitting steel tubes raised the tops of the test tubes an inch out of the furnace, placing the rubber stoppers

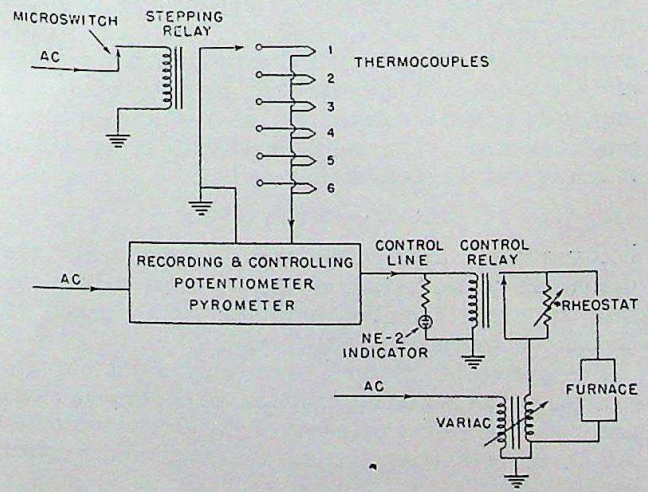


Fig. 2. Electrical circuitry.

in cool air, but copper tubing and water coolant also were necessary to extend the life of the stoppers to more than twenty hours.

The furnace insulation began to crumble under constant use, but it was found that if 85% phosphoric acid were applied to the asbestos and then the mass heated to 300°, the asbestos hardened considerably while retaining its toughness.

The final concentrations of $KClO_3$, $KClO_4$, and KCl were computed from known starting amounts with the aid of the following equations:

1. x moles $KClO_3$ + y moles $KClO_4$ = $(x + y)$ moles KCl + $[(3/2)x + 2y]$ moles O_2. Then KCl found = $x + y$ moles and O_2 lost = $(3/2)x + 2y$ moles, so
2. 4 (KCl found) − 2 (O_2 lost) = x moles = $KClO_3$ consumed, and
3. 3 (KCl found) − 2 (O_2 lost) = y moles = $KClO_4$ consumed.

A negative amount of substance consumed meant that the substance was formed. Titrations for chloride ion were made with silver nitrate. Sometimes the chromate indicator was obscured in the purple solutions, but a few drops of 3% hydrogen peroxide destroyed the purple color (excess peroxide must be destroyed by heating). A few pieces of dry ice dropped into the solution converted K_2CO_3 to $KHCO_3$ and gave a more suitable pH for titration.

A Consolidated model 21-103C mass spectrometer provided much information about the super-oxidizing gas evolved from the $KClO_3$-MnO_2 melts. The most outstanding property of the gas is its intense reactivity—it makes short work of hydrocarbons if they are used to seal joints on the spectrometer, and the resultant spectra are unintelligible. This superoxidizer is given off in appreciable amounts only if certain oxides are present, yet its amount is not proportional to the catalytic activity of the oxide. The best catalysts for oxygen evolution are the transition metal oxides; more acidic oxides produce more super-oxidizer. The super-oxidizer has an unusual effect on KI-starch paper: if the paper is dry, it is turned brown, then white again rather rapidly.

The samples of oxidizing gas were best collected (immediately after generation) in a U-tube immersed in 2-methylpentane slush at −130°C. Liquid nitrogen condensed too much oxygen, and dry ice-acetone baths were not quite efficient enough at the high rate of flow resulting from the faster decomposition which produced more super-oxidizer. A small plug of glass wool in the gas line removed small particles spewed forth by the melt.

The chlorine required for comparison of spectra was prepared from MnO_2 and HCl; and ClO_2 was prepared from 0.25 g oxalic acid and a thick paste of 1 g $KClO_3$ and water. The Cl_2O_7 was made by mixing equal quantities of 1 part $HClO_4$ + 4 parts kieselguhr with 1 part P_2O_5 + 4 parts kieselguhr. All the gases tested were used immediately or collected in U-tubes in coolants from −80°C to −130°C.

Results and Interpretations

The rate of decomposition of potassium chlorate rises with both the absolute amount and the proportion of MnO_2 employed, as shown in Table 1. The potassium chlorate in experiments 3 and 4 was only slightly decomposed at 380°, while that in experiments 1 and

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2, decomposing more rapidly, was nearly exhausted at 490°. Although 2 and 3 had nearly the same ratio of MnO_2 to $KClO_3$, 2 gave off oxygen 110° lower than 3. Number 3, with five times the concentration of MnO_2 that 1 had, as well as five times the amount, evolved oxygen slightly more than five times faster. However, 1, with the same *amount* of MnO_2 as number 2, but four times the concentration, gave off gas at 3.9/2.2 = 1.7 times the rate of 2. Apparently the MnO_2 gave rise to some slightly soluble or very unstable active

Table 1. Data for Rate of Decomposition of $KClO_3$

Expt.	$KClO_3$ (g)	Wt. MnO_2 (g)	Ratio	Rate	Temp.
1	1.5622	0.025	1/60	3.9[a]	380°
2	6.1341	0.024	1/250	2.2	380°
3	1.5687	0.005	1/300	2.2	490°
4	1.5330	0.001	1/1500	0.4	490°

[a] Rate is expressed in 10^{-3} gram molecular volumes per minute.

agent. This active catalyst is not the permanganate ion nor the manganate ion; $KMnO_4$ was found to be only 1/6 as effective as MnO_2, mole for mole, and MnO_2 + base (= manganate) was no better. In fact, addition of base even in small amounts lowers the rate of decomposition by a large factor.

Triangular constitution diagrams are used in Figure 3 for representing the initial and final concentrations of reactants. The circles on Figure 3 indicate the direction of decomposition of several mixtures of MnO_2 with $KClO_3$-$KClO_4$-KCl combinations. Oxygen

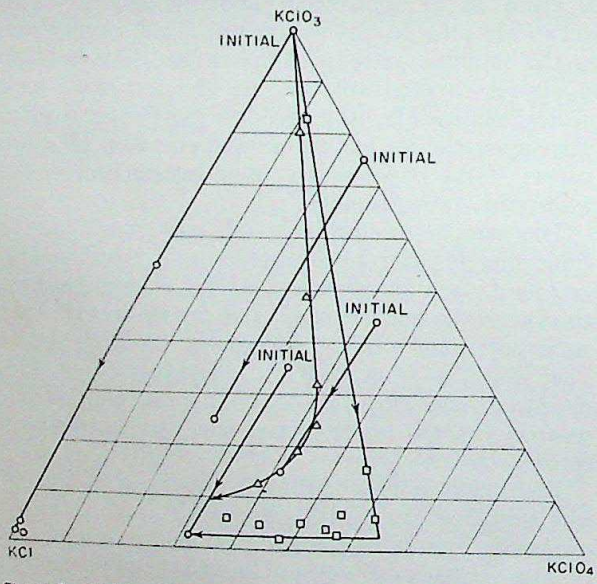


Figure 3. Initial and final composition of mixtures: ○, mixtures of MnO_2 + $KClO_3$ + KCl; □, pure $KClO_3$; △, mixtures of K_2CO_3 + $KClO_3$ + MnO_2.

comes off readily at temperatures so low that no $KClO_4$ is formed or decomposed in these reactions. Only one reaction proceeds to any extent:

$$2KClO_3 \rightarrow 2KCl + 3O_2$$

The squares on Figure 3 show the path of decomposition of pure $KClO_3$. At temperatures high enough to give an appreciable rate of oxygen evolution, the disproportionation reaction takes place readily, so that the over-all reaction is best represented by:

$$6KClO_3 \rightarrow 4KClO_4 + O_2 + 2KCl.$$

Low partial pressures of oxygen probably favor the decomposition.

The triangles on Figure 3 show the results for several mixtures with varying amounts of K_2CO_3 in $KClO_3$ + MnO_2. In general, the presence of base, even if only as $KMnO_4 (= K_2O \cdot Mn_2O_7)$ favors the decomposition of $KClO_4$, so that that which is formed at the higher temperatures required for a reasonable rate of O_2 evolution is itself more easily decomposed. This conclusion will be strengthened later.

Figure 4 is a simultaneous plot of gas evolved and of temperature, both versus time, for three reactions which differ in kind of catalyst or proportion of it. All were run simultaneously, and all show a decrease in rate of gas evolution. In all other reactions showing this slowdown, oxygen evolution also slackened at 440° ± 5°C. In Figure 4, numbers 1 and 3 had the same amounts of $KClO_3$, $KClO_4$, KCl, and catalyst, in the millimolar ratio 10:10:5:0.01, but 1 had MnO_2 while 3 had $KMnO_4$ as the catalyst. Number 2 had 12 mmoles of $KClO_3$, 8 mmoles of $KClO_4$, and 0.01

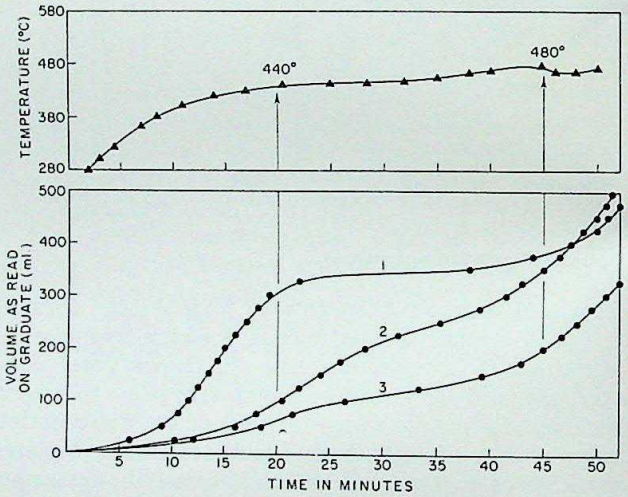


Figure 4. Course of gas evolution and temperature.

mmoles of $KMnO_4$. Since these melts solidify around 440°C from the formation of high-melting products ($KClO_3$ melts at 368°C, KCl at 776°C and $KClO_4$ at 610°C) and remelt at 480°C with attendant renewal of O_2 evolution, it appears that mobility of ions is important in the decomposition, as it is in every solid-phase reaction. The rapid solidification at 440°C indicates that the speed of the reaction:

$$4KClO_3 \rightarrow 3KClO_4 + KCl$$

becomes very appreciable then; undoubtedly the decreasing concentration of $KClO_3$ helps reduce the rate of oxygen evolution until the $KClO_4$ begins to decompose, well above 500°C.

The curves for 2 and 3 show only slight changes in slope. The persistent evolution of O_2, though slow, illustrates the slower catalysis of the decomposition of $KClO_4$ by base, strengthening the conclusion reached earlier.

Neutral or slightly basic melts were purple at all

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temperatures, but mixtures with four to ten mmoles[2] of K_2CO_3 per mmole of MnO_2 were green when molten and purple when cool; those with 15 to 40 mmoles of K_2CO_3 per mmole of MnO_2 cooled from green to blue. More basic melts were green at all temperatures. The colors varied somewhat, depending on the stage of decomposition of the $KClO_3$. If the melts cooled from green to blue or purple, the green could be restored by light heating (300°C), but would revert to the purple color upon cooling. The color change could be repeated several times before the reactants appeared to be consumed. The transition from purple (Mn^{+7}) to green (Mn^{+6}) seems to be related to the decomposition of $KMnO_4$ near the same temperature, reversing at lower temperatures because of the oxidizing action of $KClO_3$. That the blue is only a mixture of green and purple is indicated by an aqueous titration: if dilute H_2SO_4 is dropped slowly into K_2MnO_4 (stabilized by base), the green flashes with purple and gradually teaches the color of permanganate through shades of blue.

The gas evolved from the $KClO_3$-MnO_2 mixture was characterized by a complete absence of mass-spectrometer peaks at mass numbers 35, 37, 70, and 72, the characteristic peaks for chlorine. Unfortunately, no peaks appeared at the mass numbers of any of the oxides of chlorine either, but the presence of very outstanding peaks at 30.8 and 35.2 both in the spectra of the super-oxidizer and in those of pure ClO_2 and Cl_2O_7 is thought-provoking. These fractional mass peaks are probably made by transition products of metastable ions, but they could be from multiply-charged ions. Table 2 illustrates the most outstanding peaks from Cl_2, ClO_2, Cl_2O_7, and the super-oxidizer.

The peak at 44 in the fresh sample of super-oxidizer might be CO_2; the peaks at 36 and 38 in the Cl_2 sample are due to HCl. All the other peaks are not so easily explained, and in the absence of sufficient experimental data, speculation had best be postponed.

Both the dioxide and the heptoxide of chlorine were found to be sufficiently aggressive as oxidizers to turn dry KI-starch paper brown, then white, in rapid succession. Chlorine takes much longer, and the water vapor usually present in the gas begins to turn the brown iodine to the blue complex before the chlorine can bleach it white. Since the gas evolved from the $KClO_3$-MnO_2 mixtures has a rapid effect on dry KI-starch paper, it must be assumed that chlorine is not more than a part (if even a part) of the super-oxidizer. It is interesting that this super-oxidizer is evolved from such a hot source and yet does not decompose immediately.

[2] The total of chlorate and chloride and perchlorate was usually (unless otherwise noted) 25 mmoles; MnO_2 was between 0.01 and 0.1 mmale.

Table 2

Sample	Mass Numbers										
	72	70	44	40	38	37	36	35.2	35	34	30.8
$KClO_3$-MnO_2 gas, fresh			X[a]	X				X		X	X
$KClO_3$-MnO_2 gas kept at 44° for 48 hr.				X				X			X
Cl_2O_7, fresh								X			X
Cl_2O_7, kept at 44° for 48 hr.				X				X			X
ClO_2				W							X
Cl_2	X	X			X	X	X		X		

[a] The symbol *X* means present as a moderate peak; *W* indicates a weak peak. N_2 and O_2 were always present.

Summary

1. The effectiveness of MnO_2 as a catalyst depends on the amount *and* the proportions present.

2. A small proportion of MnO_2 goes into solution as $KMnO_4$, and under certain of the conditions described herein this is in temperature-dependent equilibrium with manganate ion.

3. The sudden slowdown in oxygen evolution in many experiments with $KClO_3$ is due to loss of ion mobility in a viscous or solidifying melt, as chloride and perchlorate are formed.

4. The mass spectrometer indicates the presence of chlorine oxides in the gas evolved from the decomposition of $KClO_3$ with MnO_2 as catalyst.

Acknowledgment

I should like to give my sincerest thanks to the persons who helped in this work—to Professor L. K. Nash and Dr. G. Dudek, and more especially to Professor E. G. Rochow, under whose direction it was completed.

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Chem Gems



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H. A. Buch
German Science Bulletin
American Embassy
Bonn/Bad Godesberg, Germany

German Chemical and Atomic Energy Documentation Centers

The famous handbooks by Gmelin and Beilstein have been indispensable tools for several generations of chemists all over the world. They arose from a sorely felt need for comprehensive documentation during the nineteenth century, when chemical knowledge was increasing at an ever accelerated pace. In 1817, Leopold Gmelin, Professor of Chemistry at Heidelberg, compiled a three-volume reference, which gave a detailed description of all chemicals, chemical reactions, and processes known at that time. It was based largely on an evaluation of all existing chemical periodicals. This work originally included both inorganic and organic chemistry and was kept up to date by the successive publication of new editions. The explosive growth of organic chemistry during the latter half of the 19th century eventually made such combined coverage impossible. Gmelin's handbook was then limited to inorganic chemistry, and Friedrich Beilstein started his Handbook of Organic Chemistry in 1881. This was expanded in subsequent editions until, by the end of World War I, it comprised four basic and one supplementary volumes covering all of organic chemistry to 1909. By this time both reference works had attained international recognition.

Shortly after World War I it became apparent that the Gmelin handbook could not be kept up to date with the part-time compilers and editors then utilized. This had previously also been the case with the Beilstein handbook, which enjoyed the patronage and assistance to the German Chemical Society. The massive and ever increasing chemical literature overwhelmed the inadequate staff and facilities. As the recognized representative of chemistry in Germany, the German Chemical Society (Deutsche Chemische Gesellschaft) came to the rescue of this vital enterprise. In 1921 it assumed editorial and financial responsibility for the continued preparation and publication of the Gmelin handbook. A permanent full-time editorial staff was engaged and, as the Beilstein staff before, it was installed in the Society's own "Hofmann-Haus" in Berlin, which also housed its large chemical library. Until the outbreak of World War II, work on these handbooks continued uninterruptedly. The Beilstein handbook was kept up to date by publishing a supplementary series of volumes for the decade from 1910 through 1919 and a second series from 1920 through 1929. Plans for the Gmelin handbook were completely revised in 1921–22. This resulted in an entirely new reference work of inorganic chemistry which included borderline subjects as well. It was to be kept abreast of new developments by the successive edition of exhaustive volumes dealing with a single element and all its compounds. A standardized form and systematic arrangement was developed for the presentation and referencing of the data abstracted from the literature. It was to include comprehensive physical and chemical data on the substances concerned as well as their technological applications.

During World War II, the "Hofmann-Haus" was completely destroyed, its library was saved and secured but later removed by the Soviet occupation forces first to Russia, and later to East Germany. This temporarily interrupted the documentation activities. Fortunately, however, microfilms had been made of almost the entire card file of the Gmelin documentation and had been stored in a mine in the Western zones of occupation. Thus, in 1946 work on both handbooks was gradually resumed in emergency premises. The Gmelin handbook continued at Clausthal/Zellerfeld (Harz), where many members of the editorial staff had gathered. The Beilstein Institute continued to operate in Hoechst, at the invitation of Farbwerke Hoechst, as an independent undertaking with sale of its publications providing its only financial support.

At the initiative of its director, Prof. Dr. E. Pietsch, the Gmelin Institute, however, was incorporated as a separate administrative entity of the Kaiser Wilhelm Society and of its successor, the Max Planck Society. The accommodations for the two completely independent institutes were strikingly improved when the city of Frankfurt generously erected a special new building for them. This building, completed in 1957, named the "Carl Bosch Haus" in remembrance of the first head of the Gmelin Advisory Board, is located near the Frankfurt University Campus and can accommodate both institutes (Figure 1).

Because of the Gmelin Institute's wide experience and significant developments in chemical documentation, it was commissioned by the Federal Ministry of Atomic Energy in 1957 to establish a documentation center for atomic energy. This office (Zentrale für Atomkernenergie Dokumentation—ZAED) controls and supervises all atomic energy documentation in Western Germany. A special section has thus been

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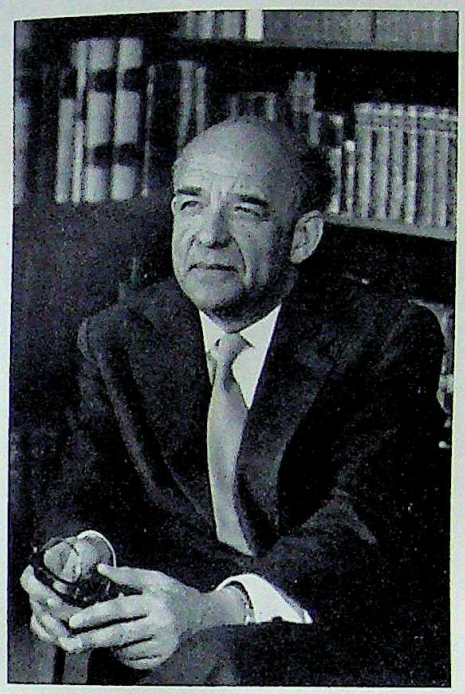
Editor's Note: This paper is based on a version which appeared first in the German Science Bulletin, 71, February, 1962, issued jointly by the Science Office at the Consulate General in Frankfort and the American Embassy in Bonn/Bad Godesburg, Germany. The gracious cooperation of Dr. Ludwig Audrieth, Dr. Herman I. Chinn, and Dr. George Bull of the U. S. Foreign Service is gratefully acknowledged.

We believe that readers will want to know the current status of the projects which mean so much to modern chemistry. We call readers' attention to a paper by Dr. Richter, the late Editor of Beilstein, in THIS JOURNAL, 15, 310 (1938), entitled "How Beilstein Is Made" and to a biographical note on Prof. Pietsch in 26, 251 (1949).

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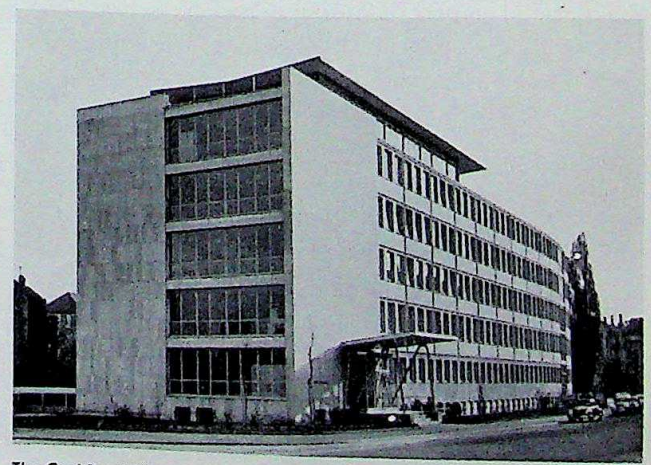
established in the Gmelin Institute, responsible for the coordination of all documentary work in this field in the Federal Republic. In addition, a separate branch office exists on three floors of an office building nearby (Friedrich Ebert Anlage) where the pertinent data are processed by scientists, and new documentation methods are developed and tested.



Dr. E. H. E. Pietsch

The Gmelin Institute for Inorganic Chemistry

The Gmelin Institute for Inorganic Chemistry and Related Fields of Interest in the Max Planck Society for the Advancement of Sciences (Gmelin Institut für anorganische Chemie und Grenzgebiete in der Max Planck Gesellschaft zur Förderung der Wissenschaften) still considers its task to be making its handbook a comprehensive yet critical summary of all inorganic chemistry. This formidable task is the responsibility of Prof. Pietsch, who has been with the Institute since 1925 and has served as its managing director since 1927. He has made every attempt to employ new, efficient, and economical methods of document processing, including machine classification and retrieval.



The Carl Bosch Haus, home of the Gmelin and Beilstein institutes.

At present, the Institute's full-time staff consists of 65 scientists (including the Institute's management, department chiefs, and editors), about 20 scientific technicians, and more than 50 persons working in a technical or administrative capacity. The scientists engaged in purely editorial duties are supported by auxiliary departments: library, documentary department, reproduction department, department for manuscript processing and proofreading, and a translation department.

The loss of the Institute's original large library during the war was a severe blow to the organization. The current library is much smaller, containing about 40,000 volumes at present. The stocks of this rapidly growing library are supplemented by an exchange system in which 2000 volumes each month are received from 320 German and foreign science libraries, such as the Library of Congress; the John Crerar Library; the Office of Technical Services (OTS), Washington; Centre Nationale des Recherches Scientifiques (CNRS); Paris; Association of Special Libraries and Information Bureaus (ASLIB), London.

This enables it to meet all reasonable demands for scientific publications on relatively short notice. Whenever possible, microphotographs are made of all pertinent matter in the borrowed publications so the permanent records are available in the Institute's archives. The library regularly receives more than 250 German and almost 600 foreign scientific periodicals. It has gained much by combining with the library of the "Zentrale für Atomkerenergie." Both libraries together comprise a total of about 1200 current journals.

The main task of the documentary department is to correlate the literature and to prepare file cards of all documentary source material. These add to the archives of similar pre-war information preserved on microfilm. It is constantly kept up to date by evaluating pertinent German and foreign periodicals, monographs, abstracting journals (including the Russian *Referativnyj Zhurnal*), and reports on specialized subjects. Today these archives contain about 2.1 million cards with 250,000–300,000 new entries added annually. Articles are indexed according to author, reference, and subject headings. For the latter, a standard system of classification has been developed, to which the processor must rigidly adhere.

The reproduction department possesses all equipment necessary to produce all normal-size and microfilm reproductions required for the Institutes' work. Here too the various units of the ZAED Information Bulletins are printed by offset, employing an electrostatic method developed in Germany (Firma Kalle) which produces the printing plates from the typewritten originals.

All members of the scientific staff have a good working knowledge of English and French. Specially trained personnel are available for translations from the Slavic languages, while translations from Chinese especially (The Institute has available about 20 journals from continental China) and Japanese are supplied by outside translators.

To cover the entire realm of inorganic chemistry demands a comprehensive classification system in which all details are meticulously standardized. The elements form the basic structural units of this system,

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with a separate volume for each. However, to allow the systematic treatment of compounds and alloys of a particular element, it has not been possible simply to follow the order of atomic numbers. Instead a classification has been adopted, in which each element is assigned a serial number which increases from the rare gases through the anion-forming elements to the cation-forming ones (*Prinzip der letzten Stelle*). A rule has been formulated that each volume bearing the serial number of a specific element shall deal also with all its compounds and combinations (e.g., intermetallic alloys) containing elements of a *lower* serial number. Thus, any compound will be found in the particular volume of the Handbook devoted to that element with the *highest* serial number of all the elements occurring in the compound.

With each volume, the specific element and its compounds are considered in a standardized manner. Descriptive text begins with the history of the discovery and natural occurrence of the element and of its compounds. The physical and chemical properties of each element are considered in turn, both from the scientific and from the technological point of view. The compounds follow in the same manner. An indication of the relative emphasis of each subject can be obtained from the following analysis:

Chemical properties	About 48 per cent
Physical properties	About 23 per cent
Occurrence	About 9 per cent
Alloys	About 8 per cent
Technology (incl. metallurgy)	About 8 per cent
Electrochemistry	About 3 per cent
History	About 1 per cent

When a volume is begun for an element not yet considered, the scientific member in charge first receives all cards concerning this element and its compounds from the documentary department. Using these references, he obtains the original publications or copies through the library. He has to study each relevant original publication to evaluate it according to the problem under review and prepare a manuscript, which is examined by the editors of the Institute. When approval is obtained from the editor-in-chief the manuscript is printed and proofread.

Between 1924 and 1961, 179 installments of the Gmelin Handbook have thus been approved for publication. This represents almost 53,000 pages of textural matter, including 8825 pages of patent registers alone. A number of supplementary volumes have also been published for several elements, to bring the basic volumes up to date. The Institute now operates so smoothly that an annual publication of 2500 to 3200 pages on the Handbook can confidently be expected for the next few years.

Atomic Energy Documentation

In principle, the documentation of atomic energy publications is handled in the same manner as that described for the compilation of the Gmelin Handbook. However, since scientific progress and industrial developments in field of nuclear energy occur so swiftly, there is a greater demand for quick publication.

For documentation purposes, atomic energy literature is subdivided into two categories, and a separate series of information bulletins is published for each. *Series AB* comprises official and semiofficial reports on atomic energy research issued by various countries, including the German Federal Republic itself. These include the reports of the United States Atomic Energy Commission (USAEC) which are received in the form of depository library supplements. The original reports are included in the Section's library and are available for microfilms and photostatic copies which can be supplied on request to any interested party. A particularly important feature of this series is the inclusion of preprints of conference reports, which the Institute receives by special arrangement from its own U. S. office in New Rochelle, N. Y. The material thus becomes available long before the full reports are published. The information given in series AB consists of the full bibliographic data in the form of so-called unit descriptors (units of information) which are arranged in alphabetical order.

Series C is a special category. It consists of monographs of specialized areas in the atomic energy field. Arrangements have been made to publish such manuscripts obtained from certain West German atomic research centers, reactor stations, and industrial plants.

The vast amount of bibliographic material processed and the desire to make such documentation rapidly available, makes some form of automatic data processing virtually mandatory. As a start, a detailed systematic schedule of information units has been established for classifying reports by subject headings.[1] Once the appropriate subject area has been determined by the responsible scientist, each of the pertinent information items is punched on an index card. The entire stack of cards is then arranged alphabetically by an IBM card-sorting machine according to subject headings. This sorted stack of cards is then scanned by another IBM machine for transfer to an electric typewriter. A manuscript sheet is thus produced representing a complete breakdown of the contents of the publication into alphabetically ordered descriptors. This manuscript sheet is finally used to produce a printing plate by the direct electrostatic method.

The Beilstein Institute for Organic Chemical Documentation

In contrast to the Gmelin Handbook, in which each volume contains a complete documentation to the time of preparation, the Beilstein Handbook covers only the material published during a specific period. The Handbook, published in 1910, consisted of four regular volumes and one supplementary volume and covered the period up to 1909. This still comprises the basic part of the Handbook. The first two supplements covering the decades from 1910 to 1919, and from 1920 to 1929 were published several years ago. The third supplement is to cover a twenty-year period, from 1930 through 1949. Although work is still in progress for this supplement, preparations are under way for the fourth supplement covering 1950 to 1959. When completed, the third supplement will comprise 27 volumes. Volumes 1–4 will deal with acyclic compounds; 5–16 with isocyclic compounds, and 17–27 with heterocyclic compounds.

[1] A special thesaurus of the descriptors used was published in the spring of 1962.

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Documentation of the third type is based on original articles published in the chemical periodicals of all countries as well as published abstracts from non-available journals. Biochemical and physical journals are utilized when pertinent organic data are included as are the contents of German and American patents relating to organic compounds.

Work on the volumes is taken up in turn. Publications to be considered are first subjected to a preliminary breakdown according to subject headings, and appropriate abstracts prepared. These are then entered in a card index which today totals about 1.5 million cards. The data for each volume are then organized and classified and the manuscript prepared.

Until his premature death a few months ago, Prof. Dr. Friedrich Richter headed the Beilstein Institute. He was a specialist both in the fields of organic chemistry and of documentation. Prof. Boit has been selected as his successor. The scientific staff of the Institute presently numbers about 65 persons.

Harold E. Brower
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A Glass Electrode *p*H Meter Using a Vacuum Tube Voltmeter

A simple *p*H meter can be constructed for less than ten dollars when used in conjunction with a vacuum tube voltmeter (VTVM) of 1.5 volt full scale sensitivity. This makes an interesting, elementary project in chemical instrumentation.

Vacuum tube voltmeters generally have an input impedance in the range of 10–22 megohms, whereas instruments using an electrometer such as a micro microammeter, ionization chamber, or *p*H meter may have an input impedance of 10^4 to 10^8 megohms.[1] Thus it was possible to construct a modular unit consisting of a single electrometer pentode with grid current of the order of 10^{-13} amperes and direct coupling this to a VTVM to provide the necessary input impedance and a slight voltage amplification of about 1.4. A CK 5886 subminiature electrometer pentode (Raytheon) was selected for its low cost ($5) and ready availability from most large electronic supply houses. Of course the accuracy of the whole unit cannot be any greater than that of the VTVM which is commonly ±3% of the full scale voltage; however, our instrument was found to be accurate to 0.2 *p*H unit and reproducible to 0.1 *pH* unit.

The electrometer tube was triode connected since this gives better linearity than the pentode connection.[2] Resistors R_1 and R_2 are to protect the grid from accidental voltages. Battery B_1 provides enough negative bias on the grid to keep the grid current at 10^{-13} amperes; if the bias becomes more positive than −1.5 volts grid current increases exponentially. Battery B_4 provides a bucking voltage so that it is possible to zero the meter with the zero adjust control on the VTVM. The grid circuit should be carefully wired to avoid leakage paths. Switch S_1 may be a source of trouble due to its capacitance to ground in an ultra high resistance circuit and also due to contact potentials.[3] Better results were obtained when the single pole double throw connection on a microphone input jack was used which puts the glass electrode into the grid circuit when the plug is inserted and switches to "standby" when it is removed. The whole assembly was placed in a 4 in. × $2^1/_2$ in. × $2^1/_4$ in. Bud "Minibox."

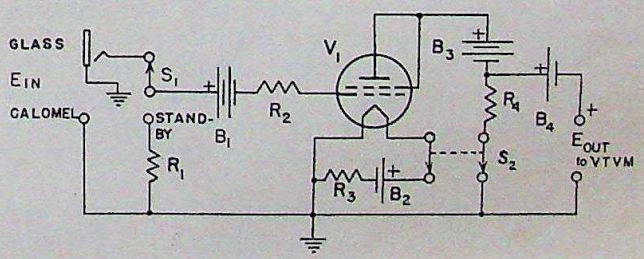
The operation and calibration of the meter was as follows: a cardboard scale was constructed and placed on the plastic meter cover. Three buffer solutions, for example *p*H 4, 7, and 9 were sufficient to calibrate the scale. The zero adjust control on the VTVM was used to center the needle at *p*H 7, with the sensitivity set at 1.5 volts full scale. It will be found that the scale is reversed from the conventional direction; i.e., *p*H units will be 14 to 0 from left to right. It can readily be shown that the potential of the glass-S.C.E. electrode pair becomes more positive with increasing acidity according to the equation $E = 0.09 - 0.059$ *p*H at 25°C, accounting for this observation.[4] No temperature compensation was employed since this would lead to an increasingly complex circuit. A change of five degrees after standardization alters the length of the entire scale 1.7%.

[1] Partridge, G. R., "Principles of Electronic Instruments," Prentice-Hall, Inc., New Jersey, 1958, p. 109.

[2] Technical Information and Transfer Curves, CK 5886, Raytheon Co., Inc., Industrial Tube Division, Newton, Mass., 1956.

[3] Partridge, G. R., *ibid.*, p. 112.

[4] Day, R. A., and Underwood, A. L., "Quantitative Analysis," Prentice-Hall, Inc., New Jersey, 1958, p. 295.



Electrometer circuit: R_1R_2, 22 meg; R_3, 10; R_4, 200 K; S_1, spdt; S_2, dpst V_1, CK 5886; B_1, 2.7 V Hg; B_2, 1.4 V Hg; B_3, 9.8 V Hg; B_4, 1.4 V.

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Technical Report Writing in Freshman Chemistry

There has been considerable criticism of the writing skill of young engineers and scientists. Whether modern students are better, or worse, in this skill than their predecessors does not appear to have been objectively measured. Any difference, if it exists, is of less importance than taking action to improve the situation. Various remedies have been proposed. Recommendations usually include a course in technical writing as an elective prior to graduation, in graduate school, or as an evening course for those who are professionally employed.[1]

The technical student should start his training in good communication techniques as early in his career as possible. Why wait until unsatisfactory habits are established before introducing him to the proper techniques of formally communicating with his fellow-workers? Although a complete course in technical writing would be difficult to include in the freshman year, it is possible to provide some training in connection with regular classroom and laboratory assignments. This represents a practical application of English, much as problem solving is a practical application of mathematics.

During the last five years, freshman chemistry students at this college have received instruction in the elements of technical writing and speaking as part of the general chemistry course. Chemistry was used for this experiment rather than the other science courses, because it reached the largest number of students. Assigned exercises during the first semester consist of preparing tables, graphs, bibliographies, and other details of technical writing in technical journal style. These exercises are worked into the regular instruction either as part of regular class assignments, when appropriate, or as a modest amount of extra-curricular homework. The special techniques are explained during class periods, and the assigned exercises are graded and criticized in recitation periods in the same manner as other problem assignments.

At the beginning of the second semester, each student is assigned a topic in industrial chemistry, metallurgy, new developments, or some other descriptive subject. He is allowed six weeks to prepare a 2000-word technical report in a style suitable for a scientific journal. The report ties together the separate exercises of the first semester and enables the student to see how the various parts combine to make an acceptable whole. The reports are graded, using an objective, self-explanatory form.

The graded reports are returned to the students, who are given about two weeks to prepare a 10–12 minute oral report on their subject. The students are encouraged to obtain specimens, arrange demonstrations, prepare suitable charts or lantern slides, or use any other appropriate methods to illustrate their talk. The presentations are given in the style of a scientific society meeting, with the instructor controlling the timing and keeping the meeting moving. The subjects were originally selected so that three related topics can be presented in one recitation period. Time is provided at the end of each presentation, or at the end of the period if the speakers so desire, for answering questions and clearing up doubtful points. Each student's presentation is graded by the instructor and by each of the students present. The grading form[2] has a space at the bottom for comments concerning the presentation. The grade sheets, after trimming off the name of the student who prepared it, are given to the speaker after the grade is recorded. The student grading sustains interest, and the comments which are made about each other's speaking techniques seem to have an important influence in correcting poor speaking habits.

A 46 page mimeographed booklet[2] has been prepared to explain and illustrate the details of preparing a technical report and presenting it orally. This booklet emphasizes basic steps which are frequently omitted in texts on technical writing and which are only mentioned briefly in the "Instructions to Authors" sections of most technical journals.

The total class time devoted to the program amounts to one period in the first semester for explaining the plan and discussing the exercises which will be assigned; two periods in the second semester, one for assigning topics and explaining the requirements of a technical paper, the other for discussing oral presentations; and a few minutes during about half a dozen recitation periods for discussing the solution of the exercises. The time required for the student presentations is the same as would be required by the instructor to present the same material.

The results of the program have been analyzed. Replies to a questionnaire sent to students over a year after completion of the course were unanimous in the opinion that the instruction had been helpful in upper class work. Several voluntary letters and personal visits have expressed appreciation for the training. The results have been so satisfactory that the program is now included as part of the freshman chemistry course at this college.

[1] Symposium: "Training Chemists and Chemical Engineers in Technical Writing," J. CHEM. EDUC., **33**, 54–67 (1956).

[2] Copies of the grading forms and sample exercises are available without charge from the Chairman, Natural Science Department, St. Petersburg Junior College, St. Petersburg 10, Florida. The booklet may be purchased from the Student Bookstore, same address, for 75 cents each, prepaid · 10 per cent discount for more than 10 copies.

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A "Direct Attachment" Kjeldahl Apparatus

The speed and reliability of the modified form of the Kemmerer-Hallett form of Kjeldahl apparatus arise largely from operative simplicity.[1,2] No quantitative transference of corrosive liquid is necessary; the digestion flask containing concentrated sulfuric acid, a catalyst, and ammonium salt formed by the destruction of the nitrogenous sample is attached directly to the distillation head by a standard-taper joint. The apparatus is all-glass and has the minimum of detachable joints. These features, highly desirable for advanced or routine work, cannot be achieved without expense. Both initial and replacement costs are therefore likely to weigh against acquisition of multiple sets needed in beginning courses in analytical chemistry.

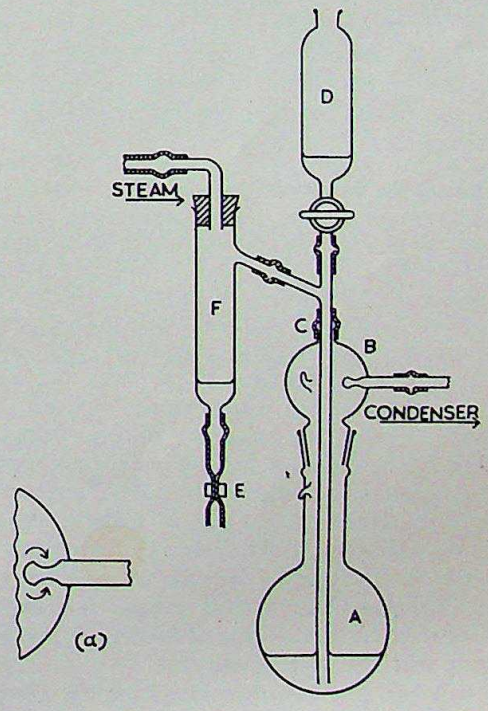
Because of the ready attack on cork or rubber by sulfuric acid, it seems that any simplified apparatus that uses the "direct attachment" principle should retain the standard-taper joint between flask and distillation head. During the distillation, this joint becomes hot and probably receives alkaline spray. While an experienced operator will remember to disconnect the joint as soon as distillation is complete, a beginner who lets the apparatus cool with the flask still attached may find the joint firmly "frozen."

No complicated or large special glass parts are involved in the apparatus shown in the figure. After completion of digestion and cooling of flask *A*, a Teflon taper sleeve[3] is slipped on the cone of distillation head *B*. The latter is then attached to the flask; two springs (not shown) stretched between sealed-on hooks prevent the joint from opening. The glass center tube, through which sodium hydroxide solution and then steam are introduced, may be slid up and down in rubber tubing sleeve *C*. This accommodates flasks that are not of identical length. Alkali is delivered from funnel *D*, which has a Teflon stopcock. When this is closed and clip *E* is tightened, steam entering as shown is forced to pass through the now-alkaline solution in *A*. Steam and ammonia pass over into the condenser; provided that distillation is not excessively rapid (the desirable rate is between 3 and 4 ml per min), spray is effectively arrested by the deflector in *B*. This is shown enlarged in (*a*); the inner end of the exit tube is closed, so that vapor must leave through two diametrically-opposed holes as shown. Trap *F*, made from a 200 × 38-mm boiling tube, prevents the contents of *A* from being sucked into the steam generator if the heating of the latter is discontinued. Release of clip *E* allows the trap to be emptied and interrupts the flow of steam through *A*.

To provide for ready use and easy dismantling for cleaning, the apparatus shown and the associated vertical condenser are mounted on a rectangle of $^1/_2$-inch thick plywood.

Dimensions are such that the bulb of flask *A*, top of funnel *D*, extremity of the steam inlet tube, and stem of the condenser below the water jacket project beyond the board. A facing of Formica or similar sheet is a desirable but not essential feature. Spring clips firmly retain *A*, *D*, *F* and the condenser; the latter is further secured by its tubulures, which pass through the board, so that water and waste connections may be made at the back Most of the joints are glass-to-glass beneath rubber tubing sleeves, as shown. Two 3-in. lengths of $^5/_8$-in. diameter hardwood dowel rod project from the back near the top and bottom of the center line. These allow the board and its equipment to be mounted in clampholders at the desired height on a heavy-based ring stand.

This apparatus was developed with the partial support of the National Science Foundation's program for the design of science teaching equipment.



[1] Kemmerer, G., and Hallett, L. T., *Ind. Eng. Chem.*, 19, 1295 (1927).
[2] Fisher Scientific Co., Catalog 59, 968 (1959).
[3] Arthur F. Smith Co., 311 Alexander St., Rochester 4, N. Y.

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Scientific Education in Ireland

Educational life in Ireland is in a transitional period. The educational system is still largely modeled on that of Britain. But the British have changed their system radically in recent years. Seven new universities have been organized in Britain in the past few years and there is a great outcry for more.

University College Dublin embodies many of the ideas of John Henry Newman about a university. It is interesting to see how his ideas have been developed and modified into the modern institution. Founded in 1851 by Newman as the Catholic University of Ireland, University College Dublin has, since the Irish Universities Act of 1908, been a part of the National University of Ireland. Officially the National University is non-sectarian, and persons of many different religions are found among the staff members and students.

A difficulty peculiar to education in Ireland is the Irish language problem. The Irish republic in the last generation or so has been making serious attempts to make Ireland into a bi-lingual country with what appears to an outsider to be indifferent success. All Irish students must study Irish (Gaelic) in school and must pass an examination in Irish in order to qualify for the Leaving Certificate, equivalent to the American high school diploma. However, relatively little Irish is spoken anywhere in Dublin. University College Dublin is relatively free from the necessity of using Irish except as a second language. At University College Galway, however, in the heart of the area where Irish is spoken as a native tongue, a student can take his entire course of instruction to the degree level in seventeen fields, including chemistry, in the Irish language.

The National University of Ireland

The granting of academic degrees in Ireland is to a large measure controlled by the National University of Ireland. The function of this institution, which has offices on Merrion Square, Dublin, is to give degrees and administer the examinations leading to these degrees. The examinations themselves are set and graded by the various constituent colleges of the university. Under its charter, dating from 1909, the National University of Ireland has three Constituent Colleges, University College Cork, University College Dublin, and University College Galway, and one Recognized College, St. Patrick's College, Maynooth. This latter institution is largely a seminary of the Roman Catholic Church, but offers courses leading to a general or honors degree of bachelor of science in chemistry, mathematics, or physics.

The colleges of the university are in Newman's words: "the corrective of the universities."[1] The idea is somewhat general and in actuality the function of the colleges can be stated quite definitely: "University College Dublin is a corporation empowered to provide teaching for Degrees and Diplomas of the National University of Ireland, and facilities for the prosecution of original research in science, literature, or other subjects, and especially in the application of science."[2] In other words, the college provides facilities for teaching and research but does not grant degrees. The granting of degrees is controlled by the university, but the examinations leading to the degrees of the National University of Ireland are set largely by the staffs of the colleges with approval by an external examiner.

University College Dublin

A student in science may work toward two types of degrees at the undergraduate level at the University College Dublin, a three-year general or pass degree, and a four-year honors degree in biochemistry, botany, chemistry, experimental physics, geology, and zoology. As a student progresses through the four year program he is exposed to increasingly more specialized teachings. If interested in chemistry, for example, he takes in his first year: chemistry, experimental physics, mathematics, and a fourth optional subject, e.g., botany. In the second year he studies three subjects: chemistry, experimental physics and mathematics. In the third year, he takes his major subject, chemistry, and a minor subject, e.g., experimental physics. The fourth year is devoted exclusively to chemistry. Studies of a general nature must be undertaken by a student on his own in his spare time, or not at all. It would seem that for the present in Ireland, one must look to the secondary schools for formal presentation of broad general education.

The Instructor

The chemistry staff consists of a professor, a statuatory lecturer, four college lecturers, and seven assistants, a total of thirteen on the teaching staff to to handle the 1143 students studying in the department of chemistry in 1961. If we consider the time spent by some students in other departments than chemistry and adjust the total number of students to an equivalent number spending full-time in the chemistry department, we obtain a full-time student equivalent of about 300. On this basis the student-staff ratio is about 300/13 or 23:1.

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[1] NEWMAN, J. H., "University Sketches," edited by TIERNEY, M., 2nd ed., Brown and Nolan, Ltd., Dublin, 1961.
[2] University College Dublin, calendar for the session 1961–2.

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If we compare this student-staff ratio with the ideal of 10:1 recommended for most universities and colleges in America, it would appear that the teaching staff is considerably overworked. Actually the work load seems light by our standards. There are several additional factors to be considered in evaluating the teaching load: the shorter teaching session; the number of actual student contact hours experienced by the average staff member—only seven; and the manner in which the lecturing is done—little tutorial work is done by the staff.

An estimate of the financial remuneration of university staff members in Ireland is difficult to make in terms comparable to that of American university professors. Salaries for professors might be well above £2000 per annum but the over-all average for the chemistry staff is more likely about £1500 per annum. If we multiply this amount by the official exchange rate of $2.80 per pound, we obtain an annual salary of only $4200 on the average. However, in comparing standards of living between Ireland and the United States, it is in many ways more realistic to use the old exchange rate of $5.00 per pound. In this case the average £1500 salary is more like $7500 in value.

The Life of the Student

The chemistry student in the Irish university does not differ in any marked way from the average American student. No student is admitted to University College Dublin who will not have attained the age of 17 years on the 15th of January of the year following entry. Entering students must pass a matriculation examination given in the summer preceding the term of entry. All students must pass in five subjects, including Irish for all students born in Ireland. Fees for students majoring in science are about £75 per session.

Very little supervision is given to students in regard to their study habits, except for the provision that attendance at three-fourths of the lectures in each class is required, and class rolls are taken at lectures. Very little, if any, work of a tutorial nature is provided, such as problem assignments or regular quizzes. The chemistry department is actually more progressive by American standards in this regard than many of the other departments, and is trying to provide some "tutorial lectures" and some periods of consultation between students and staff members at which problems can be worked out and questions asked. Irish students can be noisy and unruly when assembled in large groups, but tend to be quite shy and reluctant to ask questions when meeting in small groups. This is one of the most obvious differences between Irish and American students. It results, possibly, from the more rigid discipline exercised in Irish secondary schools which tends to inhibit individuality in students, and to encourage group exuberance.

The first year course in chemistry at University College Dublin, equivalent to the freshman course in chemistry in American universities, is described in the 1961–2 calendar as follows: Three lectures and two practical classes each week during the session.

Lectures. Fundamentals of chemical theory. Elements of physical chemistry of the gaseous, liquid, and solid states. Elementary structure of matter and the theory of valency. Periodic classification. Reaction velocity. Equilibria in homogenous and heterogenous systems. Elementary electro-chemistry. Colloids. The chemistry of more common elements from the standpoint of the periodic table. Organic chemistry including determination of molecular and structural formulae, homology, functional groups in aliphatic and aromatic systems and stereoisomerism.

Laboratory work. Preparation of pure substances. Qualitative analysis of single salts and mixtures. Volumetric analysis including acid-alkali and oxidation-reduction titrations. Simple gravimetric estimations. Semi-micro qualitative analysis. Chromatography and simple physico-chemical experiments.

The second, third, and fourth year courses in chemistry at University College Dublin are an extension of the same material listed in the first year course with lectures in theoretical, physical, inorganic and organic chemistry, and practical (laboratory) work in most of these phases. No specific number of lectures is set in any particular branch of chemistry, and the arrangement is very flexible. One lecturer or group of lecturers will take the second year students for a while in organic chemistry, for example. Then this group will finish what they consider to be a unit of work and the inorganic chemistry group will take over the second year students for a while. Of course, the staff is constantly conferring about the handling of the various classes of students, and probably more complete coverage of all topics from the professor's point of view is provided than in the American system. But the system lacks coherence, and the student is required to create order out of a heterogenous series of lectures by various people. The intellectual level of lectures is quite high and the honors degree students all have a considerable amount of research required in the fourth year.

Higher Degrees

A degree of Master of Science is awarded by University College Dublin, and may be obtained by thesis or by examination. The minimum residence requirement is one year (three terms) after the primary degree. The PhD degree may be taken after a minimum of two years (six terms) of residence following the primary degree. A thesis "worthy of publication" must be prepared under the supervision of a professor or, by arrangement, under another staff member. Examinations, both written and oral, may be required by the faculty. A reading knowledge of two foreign languages is also normally required. On the whole, the requirements for the PhD degree from the Irish universities are considerably more lenient than those of the average American university. The degree of Doctor of Science, ScD, may also be awarded to graduates of the National University of Ireland on the basis of published work *alone* at a time not less than five years after the student has obtained the primary degree.

The Future

The chemistry department of the University College Dublin is presently under progressive leadership, and is experimenting with different approaches to the teaching of chemistry. Numerous lecturers are brought in from outside Ireland, and in cooperation with the Department of External Affairs, visiting professors from the United States are in residence for periods of up to one year to provide an exchange of ideas in

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chemical education at a day-to-day level. This willingness in Ireland to take an open-minded approach to chemical education is making it the object of considerable interest in other countries. Under the sponsorship of the University College Dublin chemistry department, and the Organization for European Economic Cooperation, a seminar on the status and development of the teaching of chemistry was held in Ireland in 1959 with many visitors from abroad attending. The objectives of this seminar were to consider at a high level the revision of chemistry teaching on the basis of knowledge of the atom, the pruning of subject matter in order to give more time to modern fundamentals, and the teaching of chemical principals as an intellectual disciple.[3] In the summer of 1962 construction began on the science building on the new campus of the University College Dublin at Belfield, near the outskirts of Dublin.

Acknowledgment

I wish to express my appreciation to An Bord Scolaireachtai Comalairte, Department of External Affairs, Republic of Ireland, for the grant which, together with the sabbatical leave granted to me by the New Mexico Institute of Mining and Technology for the year 1961–2, made possible my stay as Visiting Professor of Chemistry at University College Dublin.

[3] Wheeler, T. S., *Nature*, 186, 208–10 (1960).

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Adjusting Quiz Grades to a Common Scale

In determining the final grade for each student in our large, multi-section chemistry courses we met the problem of assigning a quiz and laboratory grade to each student so that variability of grades between sections was eliminated. This problem must be common in other schools as well. The large lecture class is divided into smaller quiz-laboratory sections supervised by instructors other than the lecturer. Every student takes the same hour and final examinations. Every student does not take the same quiz and laboratory tests.

The variability of grades between sections may arise from several sources. For example, one instructor may give more difficult quizzes than another, so that the same student's grade might have been different if he had drawn another section. In addition, one section as a group may have a higher ability than another, and an average student in one section might appear to be superior in another. Because instructors tend to reflect the quality of their students in the difficulty of the quizzes and in the severity of grading, the same student might find his grade dependent upon the section. Further, a student may study carefully for the hour examinations and for the final examination, but tend to slight his day-to-day preparation, or vice versa, and his quiz grade should reflect this difference in preparation.

To overcome this variability and to find a quiz and laboratory grade which is directly comparable to the hour and final examination grades, we proceed as follows: We assume that the distribution of grades follows a Gaussian error function so that the probability of achieving a particular grade is given by (*1*)

$$y_i = \frac{1}{\sigma\sqrt{2\pi}} e^{-x^2/2\sigma^2} \qquad (1)$$

where x is the deviation of a particular grade, m_i, from the arithmetic section average grade, $\bar{m}$, i.e., $x = m_i - \bar{m}$, y_i is the probability of finding this deviation, and σ is a constant, the standard deviation. The quiz grades will give a probability curve distributed around $\bar{m}$; this distribution will be called the quiz scale. These grades are to be adjusted so that they are distributed about the section hour-final average grade, $\bar{m}'$; this distribution, for which primed symbols will be used, will be called the hour-final scale. To make this correction, we assume that the probability of obtaining a particular grade on the quiz scale is proportional to the probability of obtaining the corrected grade on the hour-final scale, so that

$$y_i = Ky_i' \qquad (2)$$

Since probabilities are concerned with deviations from the average, it seems reasonable to insist that the average grade on the quiz scale should adjust to the average grade on the corrected scale. We are requiring, then, that $m_i' = \bar{m}'$ when $m_i = \bar{m}$. By substituting this requirement and equation (1) into equation (2) we find that $K = \sigma'/\sigma$ so that equation (2) becomes

$$\frac{x}{\sigma} = \pm\frac{x'}{\sigma'} \qquad (3)$$

The positive root of equation (3) must be used so that grades which lie above average on the quiz scale will lie above average on the hour-final scale. Equation (3) shows that our assumptions lead to the requirement that the standard z score (*2*) on one scale be the same as the z score on the other scale; this again seems to be a reasonable requirement.

Equation (3) is the fundamental equation for adjusting grades. To adjust a set of grades, the ratio of the two standard deviations needs to be known as may be seen if equation (3) is rearranged to give

$$m_i' = \frac{\sigma'}{\sigma}(m_i - \bar{m}) + \bar{m}' \qquad (4)$$

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Equation (4) allows the computation of a corrected quiz grade, m_i', from the raw quiz grade, m_i, the section average quiz grade, $\bar{m}$, and the section average hour-final grade, $\bar{m}'$. In addition, if desired, equation (4) could be used to adjust all grades to some arbitrary scale, i.e., all grades could be adjusted about some arbitrary average.

The critical factor in adjusting a set of grades is the determination of the ratio σ'/σ. Although laborious, the most valid method of adjusting grades results from the computation of σ from the root-mean-square formula (*3*) for each section's quiz grades and each section's hour-final grades. Somewhat less arduous and in our experience about as valid is the determination of σ from the mean absolute deviation (*3*) instead of the root-mean-square deviation. The ratio can then be used in equation (4) to adjust the section's quiz grades to the hour-final scale. A set of grades can be adjusted about an arbitrary average by requiring that a certain fraction of the grades lie above a certain value (m_A'). For example, a set of grades can be adjusted to $\bar{m}' = 80$ with the requirement that 7% of the grades be 93 or more. The formula for accomplishing this is

$$\frac{m_A' - \bar{m}'}{2\sigma'} = \begin{cases} 1.65\ (5\%\ m_A' \text{ or greater}) \\ 1.48\ (7\%\ m_A' \text{ or greater}) \\ 1.28\ (10\%\ m_A' \text{ or greater}) \end{cases} \quad (5)$$

The σ' from equation (5) can be combined with the σ of the set of grades being adjusted to give the ratio needed in equation (4). It might be noted also that equation (5) can be used to determine the grade on the unadjusted scale above which a certain fraction of the grades (determined by the instructor) should fall. Values other than those given in equation (5) can be determined with a suitable "t" table (*4*).

The ratio of σ'/σ can be established, somewhat arbitrarily, in other ways. Three of these methods which lead to equations either commonly used or proposed by others will be considered.

Let $\sigma = \sigma'$. Equation (4) then becomes

$$m_i' = m_i + \bar{m}' - \bar{m}' \quad (6)$$

which is a simple formula requiring the addition of the factor $\bar{m}' - \bar{m}$ to each grade to adjust it to the new scale. Adding a factor, though the factor may not be the one suggested here, is probably the most common method of adjusting grades.

(*a*) *Let the fraction of grades lying between zero and* $\bar{m}$ *and between zero and* $\bar{m}'$ *be the same on both scales or* (*b*) *let* $m_i = 0$ *when* $m_i' = 0$.

Both of these requirements give the same result though the result can be obtained more easily from requirement (*b*) by substituting the zero's into equation (4) and finding $\sigma'/\sigma = \bar{m}'/\bar{m}$ which then gives the adjustment formula

$$m_i' = (\bar{m}'/\bar{m})m_i \quad (7)$$

(*a*) *Let the fraction of grades lying between* $\bar{m}$ *and 100 and between* $\bar{m}'$ *and 100 be the same on both scales or* (*b*) *let* $m_i = 100$ *when* $m_i' = 100$.

Both of these requirements give the same result though the result can again be obtained more easily from requirement (*b*) by substituting the 100's into equation (4) and finding $\sigma'/\sigma = (100 - \bar{m}')/(100 - \bar{m})$ which gives the adjustment formula

$$m_i' = [(100 - \bar{m}')/(100 - \bar{m})](m_i - \bar{m}) + \bar{m}' \quad (8)$$

Equations (4), (6), (7), and (8), each of which can be used to adjust a set of grades, will adjust these grades so that a grade at or near average on one scale becomes a grade at or near average on the other scale. Each of the four equations will give a set of adjusted grades whose average will be the desired average. The differences among the four equations occur in the way in which grades considerably above or below average are adjusted. To illustrate these differences a set of grades was adjusted to an average of 75 with each equation and the results are shown in the table. Column one gives the set of grades which is to be adjusted. This is a set of 20 grades contrived so that the average is 50, 68% of the grades fall between 30 and 70, 11% fall between 70 and 83, 11% between 17 and 30, 5% between 83 and 100, and 5% between 0 and 17. Column two shows the results of adjusting the grades with equation (4). σ was found to be 20.8 from the root-mean-square deviation. σ' was found to be 12.16 by requiring that 7% of the grades lie at 93 or above, giving a ratio of σ'/σ' of 0.585. For comparison purposes σ was found to be 19.5 from the mean average deviation which is quite close to the value obtained from the root-mean-square deviation. Column three gives the results of using equation (6), column four those from using equation (7), and column five those from using equation (8). The average for each set of grades is given at the bottom of each column. The averages are close to but not exactly 75 because some small errors were introduced by using the graphical method of computation which will be discussed below. It can be seen that each method of adjustment gives the desired average and grades at or near average on one scale are adjusted to grades at or near average on the other scale. The grades which deviate a large amount from the average, however, are adjusted quite differently. The choice of method lies with the person doing the adjusting. It is hoped that this presentation will help clarify some of the implications associated with each choice. *Personally* we prefer equation (4), though equation (8) ranks only slightly behind and requires much less labor. This preference reflects our attention to grades which lie above average, or, more significantly, near 100, since equation (4) as used here allows only 7% of the adjusted grades to lie above 93 and equation (8) corrects a grade of 100 on one scale to 100 on the other scale.

Seifert (*5*) recommends an equation which is identical to equation (8) and points out that this equation is equivalent to the graphical method used by Ehret (*6*) for adjusting grades which lie above average. Neither of these authors develops the equation nor points out completely the assumptions and limitations inherent in this method. A presentation of at least one rational method of arriving at the equation should help users of the method understand what is being done and therefore help them decide whether or not the equation is applicable to the adjustment of a particular set of grades. Seifert (*5*) also noted that equation (7) is equivalent to the graphical method used by Ehret (*7*) for adjusting grades below average. Little (*8*) compares several methods including an additive method

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which is equivalent to equation (6). Ehret's observations about the severe adjustment of low grades with equation (8) is very appropriate and his method of combining equations (7) and (8) should not be discounted. Equation (4) was not considered by these writers.

Horton (*9*) recommends a graphical method of finding adjusted grades which is in addition to the graphical and slide rule methods recommended by Ehret and Seifert. Horton's method applies to any of the methods presented here. All the methods discussed here are modifications of equation (4), the modifications being embodied in the choice of the ratio σ'/σ. As can be seen from equation (4), m_i' is a linear function of m_i with slope σ'/σ and intercept $\bar{m}' - (\sigma'/\sigma)\bar{m}$. The conversion of a set of grades can be accomplished easily by laying off the numbers zero to 100 on the abscissa and ordinate of linear graph paper. If the abscissa is used for the raw scores and the ordinate for the corrected scores, then a line can be drawn, or a straight edge laid, between the points $(0, \bar{m}' - (\sigma'/\sigma)\bar{m})$ and $(\bar{m}, \bar{m}')$. A raw score on the abscissa is then readily converted to the adjusted score on the ordinate. This graphical method (with millimeter paper—a larger scale would have given greater accuracy) was used to adjust the grades in the table and accounts for the slight errors found there.

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Results of Adjusting a Set of Grades by Each of Four Different Methods

Raw scores	Eqn. (4)	Eqn. (6)	Eqn. (7)	Eqn. (8)
3	47	28	5	51
20	57	45	30	60
28	62	53	42	64
30	63	55	45	65
38	68	63	57	69
40	69	65	60	70
43	71	68	64.5	71
45	72	70	67.5	72
47	73	72	70.5	73
50	75	75	75	75
50	75	75	75	75
53	77	78	79.5	76
55	78	80	82.5	77
57	79	83	85.5	78
60	81	85	90	80
62	82	87	93	81
70	87	95	105	85
72	88	97	108	86
80	92	105	120	90
97	102	122	146	98
av. 50	av. 74.9	75.0	75.1	74.8

Chem Ed

LETTERS

To the Editor:

The advantages of magnetic stirring have been pointed out recently (Bloomfield, J. J., this Journal, **39**, 355 (1962)). Although Wiberg[1] states, "If the reaction is to be carried out under reduced pressure and if the reaction flask is to be heated or cooled, the magnetic stirrer is not practical," magnetic stirring of liquids is useful over a wide range of temperature and pressure.

However, it must be stressed that only *seamless Teflon-covered* magnetic stirring bars should be used. Not only can the seamed plastic bars come apart at high temperature, but a violent explosion has been reported using a hard plastic-coated stirring bar (Passer, M. J., this Journal, **32**, 332 (1955)).

Lawrence P. Verbit

Bryn Mawr College
Bryn Mawr, Pennsylvania

[1] Wiberg, K. B., "Laboratory Technique in Organic Chemistry," McGraw-Hill Book Co., Inc., New York, 1960, p. 204.

To the Editor:

We enjoyed reading the article "Scientists are also Writers," in this Journal, **39**, 479 (1962), and we concur with the author's wish for good literature in science. The fact is, however, that much of today's scientific writing, while present in good quantity, is of very poor quality both in scientific content and literary form.

Without criticizing the noted scientists Dr. Goran cites, it might be pertinent to point out that quantity, *per se*, of publications is not necessarily a worthy object. We would like to believe that quality, first, should be our concern and that the personal notoriety accruant with quantity should follow as a secondary subsidiary factor. Dr. Goran has quoted the statement that, " . . . (the) amount of chemical literature which will be published in the next three years will be equal to, or greater than, all the chemical literature that has been published so far. We feel that if ten per cent of the forthcoming literature is as *significant* as the literature that has preceded it, it will be quite surprising. The "word-of-mouth" principle is, especially in academic circles, "publish or perish." There is, therefore, a pressure, applied from many quadrants, to affix one's name to as many papers as possible, regardless of content. The effect that this kind of pressure has on the individual investigator can be, and quite often is, to put out preliminary communications, letters to the editor, and notes. Yet, with a certain amount of extra effort on his

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part, and with a completion of his projected experiments, the investigator would have, in one place, all of the information for those who are interested.

We call reader's attention to a recent article by A. B. Pardee which, we feel, is applicable to this case. Dr. Pardee has formulated a law which deals with scientific publications and which he and we shall call Pardee's Law. It states that *Am. Scientist*, **50**, (2), 130–2A (1962):

$pU = Ne^{-qt}$, where $pU = -\log U$
U = uniqueness coefficient
N = number of other independent investigators publishing the same results simultaneously
t = the time, in years, between one's own first publication and the second
q = priority coefficient

It is also stated that when N approaches infinity:

$pU = pUg$, where $pUg = -\log Ug$: Ug = unimportance coefficient

We do feel, however, that

$pU = 1/pUg$, and
$pUg = Ne^{-np}$ where n = the number of different times one has published these same results with different wording, and p = the local pressure to publish or perish factor

We realize that poking fun at this problem does nothing to solve it. It is unfortunate, however, that such a mathematical representation is even considered. The editor of any publication is not the final authority, nor should he be expected to be capable of making the judgment as to whether a paper is scientifically valid or not. It is the responsibility of each individual investigator to be morally certain that what he is contributing for publication is a real contribution to the body of science. We can only hope, also, that some day granting agencies and employers will come to realize that competent research, as well as the writing of competent scientific literature, requires a great deal of time.

J. J. Carroll
R. D. Hamilton

University of Miami
Miami, Florida

To the Editor:

Two fairly recent articles in this Journal prompt the following comments. G. H. Schenk (this Journal, **39**, 32 (1962)) has discussed the determination of glycols by means of their periodate cleavage and suggests that this procedure nicely fits into the laboratory portion of a course in analytical chemistry, particularly if some knowledge of organic chemistry is a prerequisite. An interesting modification of this procedure, which has been successfully used here, is the method developed by Allen, Charbonnier and Coleman (*Ind. Eng. Chem.* (*Anal. Ed.*), **12**, 384 (1940)). In this procedure, an acidimetric titration, in which the periodic acid is titrated as a mono basic acid, follows the oxidative step and thus permits the simultaneous determination of two reactive constituents. Synthetic samples containing glycerol and ethylene glycol have been issued as student unknowns for analysis by this sequence. The analysis provides a good test of manipulative skill and the calculations provide a good exercise in stoichiometry. Class room discussion may profitably include considerations of mechanism and rates.

Alison M. G. Macdonald and William I. Stephen (this Journal, **39**, 528 (1962)) have convincingly demonstrated the semi-micro application of the oxygen flask technique for the determination of organic sulfur and phosphorus as a suitable student exercise. Our experience supports their observations. We have used the Schoniger technique in the determination of organic chlorine with considerable success to provide an illustration of this elegant method for converting the covalently bonded halogen into ionic form. The determination of the chloride may be nicely accomplished by an amperometric titration, employing very simple apparatus which the student himself assembles (see Kolthoff, I. M., and Kuroda, P. K., *Anal. Chem.*, **23**, 1306 (1951)). Because of its sensitivity, speed and relative simplicity and because it provides a good illustration of a fundamental electro chemical procedure, we find the amperometric titration to be a useful pedagogic device.

John R. Hayes

Pennsylvania State University
University Park

To the Editor:

Although the derivation of the zero point vibrational energy from the uncertainty principle is of interest, the paper by Leonard S. Levitt (this Journal, **37**, 520 (1962)) leaves the impression that the Schrödinger equation must appeal to the uncertainty principle to arrive at the conclusion that the zero point vibrational energy is $\frac{1}{2}h\nu$ when $n = 0$.

For the problem of a particle restricted to one dimensional translational energy in a container of length l, subjected to an infinite potential at the walls but zero within the container, satisfactory solutions of the wave equation are obtained for all integral values of *n except zero*. Since the energy for such a particle is given by

$$E = \frac{n^2h^2}{8\pi^2l^2}$$

the particle possesses a zero point kinetic energy.

However for a system subjected to simple linear harmonic motion, a satisfactory solution of the wave equation is obtained for each integral value of *n including zero*. Hence for $n = 0$, ψ_0 yields a satisfactory solution and therefore $E = \frac{1}{2}h\nu$.

For a particle restricted to circular motion of radius r and subjected to zero potential energy, the energy is given by

$$E = \frac{n^2h^2}{8\pi^2mr^2}.$$

Since a satisfactory equation for the wave equation is obtained for each integral value of *n including zero*, such a particle does not possess rotational energy at absolute zero.

Frank Brescia

City College of New York
New York, New York

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To the Editor:

On page 476 of the September, 1962, issue, a simplified calculation of the tetrahedral bond angle is presented. This reminds me of a similar treatment which we heard in our lectures at Graz and which gives this angle directly. It is based on an application of the principles of vector calculations, viz., that the scalar product of two vectors is given by the product of their lengths times the cosine of the angle between them.

Starting from the same point as Dr. McCullough, we may write r_1, r_2, r_3, and r_4 for the four vectors of the C—H dipole moments; and because the dipole moment of methane is zero, we get

$$r_1 + r_1 + r_3 \cdot r_4 = 0$$

If we multiply with one of those vectors, say r_1, we get

$$r_1 \cdot r_1 + r_1 \cdot r_2 + r_1 \cdot r_3 + r_1 \cdot r_4 = 0$$

If we designate a as the length of all four C—H moments and α as the tetrahedral angle, we have immediately

$$a^2 + a^2 \cdot \cos\alpha + a^2 \cdot \cos\alpha + a^2 \cdot \cos\alpha = 0$$

which simplifies to $3 \cos\alpha = -1$

hence, $\cos\alpha = -1/3$

This means that the angle must be between 90 and 180° (more than 180° would be identical with an angle measured the other way around, and it would then be smaller than 180°) and so we find the same value of 109° 28′. This treatment, which is in fact equivalent to the one above, shows more elegantly the equivalence of all four C—H bonds.

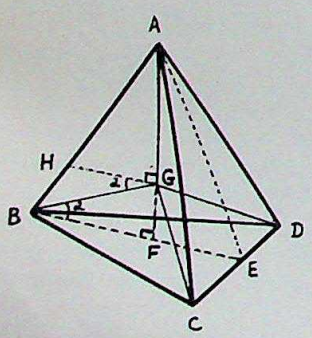
G. Snatzke

Organisch-Chemisches Institut
Universität Bonn, West Germany

To the Editor:

In the September, 1962, issue, T. McCullough (this Journal, **39**, 476 (1962)) gave a mechanical derivation of the tetrahedral bond angle. A very simple derivation follows from an elementary property of the tetrahedron, namely that the centroid divides each median in the ratio 3:1.

In the diagram, AEB is a plane which contains the centroid G, the two bonds GA and GB, and the line GH. AGF is a median of the tetrahedron. $< AGH = < AFB = 90°$. $< HGB = < GBF = \alpha$.



$$\sin\alpha = \frac{GF}{GB} = \frac{\frac{1}{3}GA}{GA} = \frac{1}{3}$$

$$\therefore \alpha = 19° 28'$$

$$\therefore < AGB = 109° 28'$$

B. L. Cockburn

Wellington College
Wellington, New Zealand

To the Editor:

Textbook errors can be psychological as well as chemical. For example, in the reaction between dilute sulfuric acid and zinc, hydrogen gas is liberated. Under certain conditions we have been able to detect measurable amounts of hydrogen sulfide gas in the hydrogen. For the beginner in chemistry, the important product is hydrogen. It would be a psychological error to detract from the main reaction and the accompanying introduction to the activity series by calling attention to the side reaction or reactions.

The point made by Bostrup, Demandt, and Hansen in Textbook Errors, 41, The Thermal Decomposition of $KClO_3$, **39**, 573 (November, 1962) is quite comparable. The catalyzed decomposition of $KClO_3$ does indeed produce several side reactions, and the liberated oxygen is far from the pure colorless, odorless gas the textbook described.

On the other hand, it would be a psychological error to draw the student's attention from the essential path of the reaction. Let him learn for the first time about the effect of a catalyst without cluttering up a big idea by calling attention to side reactions.

E. Gerald Meyer
New Mexico Highlands Univ.
Las Vegas, N. M.

Elbert C. Weaver
Phillips Academy
Andover, Massachusetts

Editor's Note: Readers should turn to p. 78 for more information on the subjects discussed in these letters.

To the Editor:

The article, "The Thermal Decomposition of $KClO_3$" in the November, 1962 Journal came at a very opportune time. The Chemistry Club was organizing a program on the topic, oxygen, for the next meeting.

Two test tube generators were set up with equal weights of high grade potassium chlorate. One was mixed with reagent grade MnO_2 and the other with the same weight of the technical grade.

The gases from each were collected in bottles placed in 2 liter beakers containing the same volume of a dilute solution of KI and starch.

The evolution of oxygen from the generator with the impure catalyst was rapid even with less heat than applied to the generator with pure chemicals. The solution colors in the collecting beakers contrasted markedly. The solution in the beaker using the pure chemical was a pale blue. The other solution was an intensely dark blue.

A comparison of the amount of chlorine liberated could be made by diluting the darker solution to match the lighter one.

Others may use or modify this experiment. It shows that the technical grade MnO_2 has greater catalytic power and also liberates more chlorine and/or chlorine dioxide in the decomposition of the potassium chlorate.

Bernard Jurale

Cheshire, Academy
Cheshire, Connecticut

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Proceedings of the

California Association of Chemistry Teachers

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Kinetics in the Study of Organic Reaction Mechanisms

Since the emergence of chemistry as a modern experimental science, chemists have become increasingly interested in the detailed manner in which chemical transformations occur. That is, chemistry is concerned with the mechanisms of reactions as well as with a knowledge of their starting materials and products.

There are a number of reasons for this preoccupation with reaction mechanisms. A knowledge of mechanisms aids the synthetic chemist in predicting by-products and improving reaction conditions, helps the analytical chemist in choosing optimum conditions for analytical procedures, and provides a powerful tool for the biochemist studying the chemical basis of physiological processes. Reaction mechanisms also provide a systematic basis, exploited particularly by organic chemists, for classifying chemical reactions and predicting chemical properties.

The increasingly important role of mechanisms in organic chemistry is attested to by the number of excellent textbooks and monographs dealing with organic reaction mechanisms (*1–3, 6–9*). Since the following discussion is concerned only with the rationale of mechanisms studies, specific examples are omitted. References *1–9* provide an excellent guide to the original literature dealing with the mechanisms of specific reactions.

A chemical reaction mechanism may be thought of as a motion picture of all of the atoms (and their electrons) involved in the reaction, beginning before the reacting species approach each other, picturing their paths during the reaction, and ending after the products have been formed (*1*). Such detailed knowledge of the course of a reaction can never be attained in actual practice, and a reaction mechanism is usually understood to mean all of the simple reactions involving molecules, radicals, and ions, that take place simultaneously or consecutively in producing the observed over-all reaction (*2*).

The experimental elucidation of reaction mechanisms poses some very thorny problems. A knowledge of the stoichiometry of a reaction, or of the position of an equilibrium, yields no information on how the reaction occurs or how the equilibrium is attained. Chemical thermodynamics, dealing as it does with initial and final states, tells nothing about the paths connecting these states. Since the individual molecular collisions and interactions comprising a mechanism cannot be observed directly, their occurrence and nature must be deduced from indirect evidence of various kinds.

The most powerful tool for the experimental study of reaction mechanisms is chemical kinetics. Kinetics deals with the rates at which chemical reactions occur, and with all of the factors which influence these rates, No reaction mechanism can be considered to be more than a temporary working hypothesis until it is supported by kinetic data (*3*).

Like any other tool, chemical kinetics has certain fundamental limitations. For those who plan to use kinetic methods in the study of mechanisms, an understanding of these limitations is highly desirable. Many chemists who had only a brief introduction to reaction kinetics during their formal education fall into the trap of misinterpreting (or, more commonly, overinterpreting) kinetic data. What, then, are some of the things that can, and cannot, be learned about a reaction by studying its kinetics?[1]

Perhaps the most useful information furnished by a kinetic study of a reaction is its rate equation. This is an equation, derived from rate measurements, which describes the concentration dependence of a reaction. For a generalized reaction:

$$aA + bB + cC + \ldots \rightarrow \text{products}$$

$$\text{rate} = -dc_A/dt = k a_A^l a_B^m a_C^n \ldots \quad (1)$$

where a_A, a_B, etc., refer to the thermodynamic activities

[1] Since the main concern here is the strategy and limitations of kinetic studies, detailed examples of techniques and principles are omitted. There are a number of excellent books dealing with the study of reaction mechanisms which may be consulted for detailed discussions of kinetic methods (*1–9*). The discussion of interpretation of rate data by Bunnett (ref. *9*, p. 177) should be of particular interest to all serious students of reaction mechanisms.

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of species A, B, etc., and c_A, c_B, etc., their concentrations. Often, the activities are approximately equal to the concentrations, and

$$\text{rate} = -dc_A/dt \cong kc_A^l c_B^m c c^n \ldots$$

l, m, and n . . . are the powers to which the activities or concentrations must be raised in order to describe the experimental observations. Since many reactions involve two or more steps, and since the slowest step (or steps), which determines the rate of the reaction, may not involve all of the starting materials, it is not generally possible to deduce the rate equation from the stoichiometric equation of the over-all reaction. Changes in experimental conditions may alter the rate equation, but the altered form is usually more general, and includes the original equation as a special case—unless the changes were sufficiently drastic to cause the reaction to proceed by a different mechanism.

The over-all *order* of the reaction described by equation (1) is $(l + m + n + \ldots)$. If a reactant (the solvent, for example) is present in large excess, rate measurements will not establish the order of the reaction with respect to it, and the observed order may be smaller than the true order.

More useful in mechanisms studies than the observed kinetic order of a reaction is its *molecularity*. Molecularity is usually defined, by organic chemists, as the number of molecules (using the term to include ions and radicals) which undergo valency changes in the slowest step of the reaction.[2]

The principal limitation of reaction kinetics in mechanisms studies is that the experimental rate equation cannot be depended upon to establish the molecularity of the rate-limiting step of the reaction. It will do so only if there is a single rate-limiting step which is not preceded by rapid equilibrium steps, and if none of the reactants in the rate-limiting reaction are present in large excess. These conditions are not always satisfied.

The rate equations for the unimolecular and bimolecular mechanisms of nucleophilic substitution illustrate this point (*8*). The bimolecular mechanism involves a concerted replacement of the leaving group by the attacking nucleophile—that is, molecules of the two reactants must collide in order for reaction to occur:

$$\text{Y:} + \text{R—X} \rightarrow \text{Y—R} + \text{:X}$$

The rate of the reaction depends on the concentrations of both RX and Y, and second-order kinetics are usually observed:

$$\text{rate} = k[\text{RX}][\text{Y}]$$

If, however, the nucleophilic reagent Y is present in such large excess that its concentration remains practically constant during the reaction (as would be true if Y is a solvent molecule), the reaction follows first-order kinetics:

$$\text{rate} = k'[\text{RX}]$$

The unimolecular mechanism of substitution involves preliminary ionization of RX:

$$\text{RX} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \text{R}^+ + \text{X}^-$$

$$\text{R}^+ + \text{Y}^- \xrightarrow{k_3} \text{RY}$$

Application of the steady-state approximation (*2* and *6*) leads to the following general rate equation for this mechanism:

$$\text{rate} = \frac{k_1[\text{RX}]}{(1 + k_2[\text{X}^-])/k_3[\text{Y}^-]}$$

The experimentally observed rate equation will depend on the relative values of k_2, k_3, $[\text{X}^-]$, and $[\text{Y}^-]$. If $k_3 >> k_2$,

$$\text{rate} = k_1[\text{RX}]$$

and first order kinetics are observed. If $k_3 << k_2$,

$$\text{rate} = k_1k_3(\text{RX})(\text{Y}^-)/k_2(\text{X}^-)$$

In this case, if X^- is present in the reaction medium in large enough amount so that (X^-) remains practically constant during the reaction,

$$\text{rate} = k'(\text{RX})(\text{Y}^-)$$

and the reaction follows second order kinetics! In short, there is no necessary correspondence between molecularity and observed kinetic order.

The experimental rate equation of a reaction also *may* establish the composition of the transition state for the rate-limiting step of the reaction. It fails to do this, however, in the case of reactions not having a single rate-determining step. When two or more slow steps of similar rates are involved in a reaction, complicated rate equations are usually obtained which tell neither the molecularity nor the composition of the transition state of any individual step in the mechanism. Even for reactions having a single rate-determining step, the rate equation will not tell how the transition state of this step was assembled, what its structure is, or what happens after the rate-determining step. For example, general acid-catalyzed reactions of a substrate S obey equally well the rate laws:

$$\text{rate} = k(\text{S})(\text{H}^+)\sum_i(\text{A}^-)_i$$

$$\text{rate} = k'(\text{S})\sum_i(\text{HA})_i$$

and

$$\text{rate} = \text{k}''(\text{SH}^+)\sum_i(\text{A}^-)_i$$

due to the fact that:

$$(\text{H}^+)(\text{A}^-) = K(\text{HA}) \text{ and}$$
$$(\text{SH}^+) = K'(\text{S})(\text{H}^+)$$

All of these rate equations indicate that the transition state of the rate-determining step of the reaction contains S and the components of the acid HA. (It may also contain one or more solvent molecules.) The rate equations do not tell whether the observed reaction involves an attack by A^- on SH^+, a slow proton transfer between S and HA, or some other process which can bring together S, H^+, and A^- into a transition state. Equivalent, but apparently different, rate laws for a reaction are found whenever preequilibria exist between two or more reactants, or between reactants and catalysts (*10*).

In summary, the rate equation *may* indicate the

[2] Physical chemists usually define molecularity as the number of molecules (ions, radicals) entering into the transition state of an elementary reaction, i.e., any one step in the overall reaction.

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composition of the transition state of the rate-limiting step of a reaction. It will *not* do so if one of the reactants is present in large excess, or if the reaction does not have a single rate-limiting step. The rate equation *may* also indicate the molecularity of the reaction, but will *not* in cases where rapid preequilibria are involved. Furthermore, the rate equation yields no information on the structure of the transition state of the rate-limiting reaction, or on the number and nature of any fast steps which precede or follow the rate-limiting step.

If the rate equation of a reaction cannot be relied upon to establish either the order or the molecularity of the reaction, and tells nothing about fast steps or transition state structures, why bother to make the kinetic study in the first place? The answer to this question lies in the fact that the kinetic data exclude all mechanisms from which the observed rate equation cannot be derived. In other words, *the chief utility of reaction kinetics in mechanisms studies lies not in establishing the correct mechanism, but in ruling out all of the possible mechanisms which are inconsistent with the kinetic data.*

In the examples used above, it was assumed, as is common practice, that concentrations and activities of reactant species are the same. This is not usually the case, except in extremely dilute solutions or in the gas phase at low pressures. A rigorous treatment of the kinetics of reactions occurring in nonideal systems requires a knowledge of the activity coefficients as well as the concentrations of reactants and catalysts. The necessary thermodynamic data are difficult to obtain, and are rarely available from the literature. The exploitation of accurate activity data in mechanistic studies of reactions in solution may provide one of the few kinetic methods of determining the role of the solvent in reactions (*11*), and should provide a sounder theoretical basis for several empirical correlations between reaction mechanism and the effect on reaction rates of solvent acidity, basicity, and ionizing power.

Much useful information regarding the mechanism of a reaction can be obtained by studying the effects of environmental changes on reaction rate. Changes in reaction rate produced by changes in solvent polarity, nucleophilicity, and ionizing power yield useful information on the role played by solvent molecules in a reaction. The effects of solvent polarity and of dissolved electrolytes on rates often yield information regarding the separation and distribution of electrical charge in the transition state of the rate-limiting step in a reaction mechanism. Changes in rate caused by changing the isotopic composition of the solvent are also instructive. For example, the measurement of rates of acid-catalyzed reactions in water and in deuterium oxide provides a useful empirical tool for studying the mechanism of acid catalysis (*12*).

Another widely used application of chemical kinetics is the study of rate changes produced by structural alterations in one or more of the reactants. A knowledge of the effects of such changes on reactivity and on the rate equations of reactions is particularly useful in the study of organic reactions. Rate variations caused by structural alterations in the reactants yield information on the electronic and steric requirements of the reaction which is pertinent to its mechanism (*13*).

A special kind of structural change which frequently causes meaningful rate changes is isotopic substitution. For example, the effect on rate of replacing hydrogen by deuterium at or near the reaction site in an organic molecule affords valuable information on the mechanism of the reaction and on the structure of the transition state (*14*).

One of the most important, and least exploited factors determining reaction rate is temperature. Most reactions are found to obey the Arrhenius equation,

$$k = Ae^{-E_a/RT}$$

quite well over limited temperature ranges. (A is the "preexponential factor," and E_a is the activation energy of the reaction.) It is easy to evaluate A and E_a from experimental rate data. These quantities—and the enthalpy ($\Delta H^{\ddagger}$), entropy ($\Delta S^{\ddagger}$), and free energy ($\Delta F^{\ddagger}$) of activation, derived from them by application of the transition state theory of chemical kinetics (*6*)—are extremely useful in mechanisms studies. They often indicate whether a reaction is unimolecular, bimolecular, or intramolecular, and frequently give hints on how the transition state is assembled. The observed values of E_a and A are often compatible with some of the possible mechanisms suggested by the rate equation, and incompatible with other mechanisms. Also, a sharp departure from linearity in the Arrhenius plot of log k versus $1/T$ is good evidence that a reaction involves two competing mechanisms.

The effects of catalysts and inhibitors on reaction rates are of fundamental importance in mechanisms studies. A knowledge of the kinds of things which catalyze or inhibit a reaction usually enables one to decide whether the reaction proceeds by a radical or a heterolytic mechanism. The influence of light and of solid surfaces on the rate of a reaction is also pertinent to its mechanism. The detailed nature of the catalysis is also important. For example, whether a reaction is general or specific acid catalyzed tells something about the proton transfers responsible for the catalysis, and the way in which the rate of an acid catalyzed reaction varies with solvent acidity gives important hints on the nature of the rate-determining step of the reaction (*15*).

And finally, measurement of the variation of reaction rate with pressure at high pressures is becoming a useful tool in the study of reactions taking place in solution. The volume of activation of a reaction occurring in the liquid phase yields information about the structure of its transition state, and hence about its mechanism (*16*).

There are, of course, many kinds of information other than rate data which are useful in the study of mechanisms. Physical measurements involving absorption spectroscopy, nuclear magnetic resonance spectroscopy (*17*), electron paramagnetic resonance spectroscopy, and cryoscopy have been valuable in establishing the existence and structures of reactive intermediates (*18*). Isotopic labeling often makes it possible to determine the role of individual atoms in reactions, and has been extensively used in establishing the positions of bond cleavages (*19*). Isotopic exchange

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experiments have served to establish the existence of several reactive intermediates (*20*). A knowledge of the structures of all of the products of a reaction, and of its stereochemistry, frequently supports some mechanisms and eliminates others from consideration. Competition and crossover experiments may furnish valuable mechanistic clues.

It is fairly easy, after a little practice, to derive a rate equation from a postulated reaction mechanism, and to predict the effects of structural and environmental changes on the reaction rate which should be observed if the mechanism is correct. Comparison of these predictions with experimental observations is a necessary step in checking the reasonableness of a proposed mechanism. The reverse of this process, arriving at a reasonable mechanism consistent with all of the experimental facts, is more difficult. Skill at this kind of inductive reasoning requires intuition, imagination, and chemical sophistication.

Chemists—particularly organic chemists—frequently publish reaction mechanisms without offering evidence to support them. Speculation is fun, and serves the purpose of stimulating thought and suggesting new experimentation. But it should always be recognized for what it is. The minimum evidence required to give credibility to a mechanism in most cases is the stoichiometric equation of the reaction, its rate equation, and its energy and entropy of activation. The more kinetic and non-kinetic data the mechanism accounts for, the greater the probability that it is essentially correct.

Mechanisms—like other scientific hypotheses—are extremely useful even though inherently unprovable. As Hammett pointed out (*6*), "A mechanism . . . . is a scientific tool by which to obtain verifiable relationships between measurable quantities; it is to be judged by its utility in correlating known facts and predicting new ones, not by its agreement with some absolute, unknowable truth."

Acknowledgment

The author is grateful to Dr. G. O. Pritchard for helpful criticisms of an earlier version of this article.

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Choosing That Science Project

A guiding principle in selecting a subject for a science project might be: *Ask a single, simple question of the world in which you live.* For example, Why does this reaction happen? What will happen if I change from blue to red light? How can I test this statement in my textbook?

The biggest problem of all for many youngsters is finding information about their chosen subjects. The process that we recommend can be summarized as follows:

First use a dictionary, an encyclopedia, and elementary textbooks *to get general background information about your subject.* What you read in these reference books will suggest specific subjects for projects and help you to *narrow your project to one you can do in the time available.* When you have decided just what questions you are going to ask of your world—just what will be the single, simple subject of your project—then go to the next step.

Use a library's card catalogue to find advanced and specialized books, looking under the various categories and names suggested by your earlier reading. To find the most recent information on your subject, you must look into magazines. The Reader's Guide to Periodical Literature, in most libraries, is your index to the more popular and simple magazines. Highly technical magazines are indexed in the Applied Science and Technology Index, available only in the large libraries, but the annual indexes of each magazine will help you.

Magazine articles have the pictures and diagrams that many students want for projects. Old copies of magazines can be bought from the publishers or from back number dealers whose addresses may be obtained from a librarian.

Quoted from the "How to" Corner by Edward Pearce in the Fall 1962 *Newsletter of the Museum of Science*, Boston, Mass.

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Report of the **New England Association of Chemistry Teachers**

Robert H. Dalton
Corning Glass Works
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Recent Developments in Glass

This is an age of rapid scientific progress in many fields. Glass technology is no exception. The recent developments in the field of glass have been so numerous and diverse that any attempt at comprehensive coverage in a brief article such as this would be so superficial as to be of little value. This discussion will deal only with a few representative examples of these recent developments which are important and of special interest to chemists.

Before starting on these recent developments, however, a brief look at the past will be of interest to chemists. Glass making is one of the oldest chemical industries. There are reliably dated specimens that go back 4000 years and no doubt the real beginnings were much earlier. One of the first products was ornamental jewelry, and this is still a flourishing business—a remarkable record for the survival of a product. As the uniformity, durability and clarity improved, glass was used in urns, vases, drinking vessels, bottles, windows, etc. Because of the comparatively durable nature of glass, a number of examples of early glass have come down to us. The first topic deals with some recent and very interesting discoveries regarding the chemical attack on these old glass items.

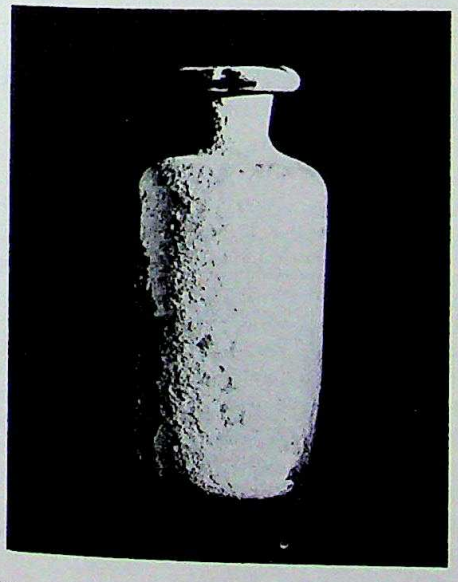


Figure 1. A Roman bottle from the first century A.D.

A New Look at Old Glass

Anyone who looks at archaeological specimens of glass in a museum will soon notice that many are coated with a crust of weathering products. Figure 1 shows such a specimen, a Roman bottle of around the first century A.D. The old glasses were in general of the alkali-lime-silicate type with a rather high content of sodium or potassium and were rather susceptible to hydrolytic attack. Through the years of exposure the alkali and alkaline earth elements were gradually leached out of the glass leaving behind a residue that consists largely of hydrated silica. Figure 2 shows a piece of the neck of a bottle of early American glass



Figure 2. Neck of bottle (American) from the seventeenth century.

(seventeenth century) that was excavated in 1959 at Kingston, Massachusetts. A thick white crust is clearly visible.

If we look at a cross section of such a crust under high magnification (Fig. 3), we find that it is not just a simple uniform layer but is almost always stratified; that is, it consists of a series of very fine layers, more or less parallel to the glass surface. These layers are only of the order of a micron in thickness and the whole picture would represent less than a tenth of a millimeter. It was first suggested that this pattern was a type of Liesegang ring phenomenon, but Brill and Hood (*1*) at Corning conceived the idea that it might result from a cyclical factor in the chemical attack such as could be caused by annual variations of temperature

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or moisture. To check this theory they have counted the strata on a number of specimens of more or less well-established history. The results are shown in Table 1. In general, there is good agreement between the dates calculated by counting layers and those known from historical records or other evidence. We thus have a new method of dating ancient glass pieces,

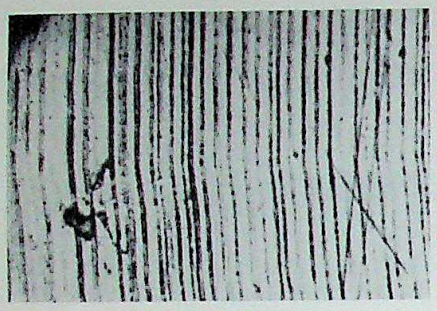


Figure 3. Photomicrograph of corrosion layer on glass.

or at least determining the period of exposure. The method will also be useful in establishing the age of archaeological sites and may even serve as a source of information about the weather in ages past. In some ways it is analogous to the well-known method of counting tree rings, although with glass, the time sequence is reversed, that is, the latest layer is on the inside. Obviously, not all samples of ancient glass will be amenable to this dating method. In many cases it turns out that part of the crust has been lost either by

Table 1. Dating of Ancient Glass

Sample	Date based on archaeological evidence	Excavation date	Layers counted	Date calculated for onset of weathering
J-5	Submerged 1781	1935	150-156-170	1765-1779-1785
J-4	Buried 1639-1670	1935	256-266-273	1662-1669-1679
J-6	Buried ca. 1660-1675	1935	261-271-286	1649-1664-1674
J-2	Submerged ca. 1600-1640	1956	295-310-320	1636-1646-1661
Pl-1	Buried 1676 or later	1959	259-269-289	1670-1690-1700
PR-5	Submerged 1692	1959	258-268-274	1685-1691-1701
SA-2	Submerged 1621	1959	319-334-349	1610-1625-1640
N-4	Manufactured eighth-tenth century	ca. 1950	930 ± 30	A.D. 1020 ± 30
N-9	Ninth-thirteenth century	ca. 1950	775 ± 20	A.D. 1175 ± 20
N-11	Ninth-thirteenth century	ca. 1950	810 ± 25	A.D. 1140 ± 25
S-1b	Late third—early seventh century	1960	1582 ± 10	A.D. 378 ± 10

accident or by overzealous cleaning. Also in some cases the cyclical factor is not strong enough to give layers that can be accurately counted. However, in spite of these difficulties, it represents a novel and valuable tool in helping us to establish our record of the past.

Flame Formed Glasses

Since chemists are often concerned with the purity of materials, the second general topic that I have selected has to do with some special glasses made by a new process which permits the attainment of extremely high purity. As you know, the conventional method of making glass consists of fusing together an intimate mix of the raw materials (usually sand, soda and limestone) in a refractory unit such as a pot or tank. In contrast, the starting point for these glasses is not ordinary mineral substances which cannot generally be obtained in a very pure form, but synthetic chemical products which can be refined by chemical means to a very high degree of purity. The manufacturing process for these glasses is also unique in that the materials are not fused in a refractory container, but are formed in the gas phase and deposited without contact with other solid materials. The method consists in feeding very pure compounds of the de-aired glass forming elements through a flame which converts them to minute fused droplets of the oxides. When these impinge on a surface they build up a layer of glass much as a layer of ice builds up during a sleet storm. Some of the compounds which lend themselves readily to this process are shown in Table 2. The reaction, in all cases, is one of hydrolysis with the water vapor in the flame.

Other volatile compounds may be used instead of the halides. In fact this has the advantage that we then get away from the halogen acids which are always a nuisance. However, the cost factor usually favors the halogen compounds. It should be pointed out that the last two materials shown in the table will not form

Table 2. Flame Reactions

$$SiCl_4 + 2H_2O \rightarrow SiO_2 + 4HCl$$
$$2BF_3 + 3H_2O \rightarrow B_2O_3 + 6HF$$
$$2AlCl_3 + 3H_2O \rightarrow Al_2O_3 + 6HCl$$
$$TiCl_4 + 2H_2O \rightarrow TiO_2 + 4HCl$$

glasses by themselves, but only when used in conjunction with one of the prior materials.

The principal commercial interest at present centers on the first reaction which is being used for the preparation of a very high purity SiO_2 glass. The principal properties of this material are listed in Table 3. The low impurity level makes it useful as a container for melting super high purity semiconductor materials. The transmission in the far ultraviolet is greatly superior to other glasses, as is the resistance to discoloration by high energy radiation. Surprisingly

Table 3. Properties of High Purity SiO_2 Glass (Code 7943)

SiO_2	99.99+%
B_2O_3	< 1 ppm
Alkalies	<10 ppm
H_2O	1 to 10 ppm

Very high ultraviolet transmission — 85%/mm at 185 mμ
Very low acoustic attenuation.
Resistant to X-ray discoloration.

enough, the acoustic attenuation is extremely low, about $^1/_{50}$ that of ordinary glasses. In fact the principal commercial application is in acoustic delay lines for electronic circuits. Optical mirror blanks are also being laid down out of this material and have been made up to 62 in. in diameter. Another interesting and important application of this product is in the nose cone of the ICBM where a high melting material is essential to the type of ablation behavior needed for reentry, and where the superior electrical properties are needed for radar transmission.

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Glass Ceramics

The next materials that we shall discuss are, strictly speaking, not glasses at all, but ceramics. However, they are made from glasses so we can justify their inclusion on this basis. Not only the materials themselves are interesting, but also the developments that led up to them. Many of the intermediate stepping stones were interesting products in themselves.

The story starts with photosensitive glass. It has been known for many years that light affects glass. Probably the most familiar example of this action is the purple coloration that some glass develops on long exposure to sunlight. It is the result of the photochemical action of the sunlight on the manganese present in the glass. This type of photosensitivity or solarization is noticeable in old windows and is often a nuisance in that newly installed pieces do not match in color. On the other hand the changes are too slow to make the process of any practical value for producing pictures in glass. About 25 years ago a new type of photosensitive glass was discovered at Corning (*2*). In this glass, brief exposure to light in the near ultraviolet gives a latent image which can be developed on subsequent heat treatment. Due largely to the work of Dr. Stookey (*3*), this process was developed into a practical method of making colored transparencies in glass and represented the first step toward glass ceramics. The pigment material in these glasses is gold with cerium added as a sensitizer. By varying the exposure it is possible to develop colors which range from blue through purple to red. These colors are believed to be due to colloidal particles of metallic gold and are suggestive of the colors obtained with colloidal gold in aqueous solutions. Figure 4 shows some pictures made in this photosensitive glass.



Figure 4. Pictures in photosensitive glass.

In addition to color transparencies it is possible to make photosensitive glass in which the image forming material is white and scatters light. To do this, the photosensitive glass is saturated with a suitable white solid. The metallic particles formed by the mechanism mentioned previously then act as nuclei on which the opal material precipitates. Silver turns out to be the best material for nucleation, and sodium fluoride is used in most cases for the white precipitate. One application of this form of photosensitive glass is in producing a marbleized pattern for facing of buildings. Examples of this use may be seen at the Glass Center in Corning, New York, and at the United Nations buildings in New York City. Another application of the opal glass is for lighting fixtures. Here opal planes or shutters are formed within the glass so that the light will pass through only at certain angles. It is something like a venetian blind inside the glass.

In the products so far described, the crystal phase has been a minor part of the total glass. However, by choosing appropriate compositions, a large proportion of the glass can be converted to the crystalline state, and this leads to still another type of photosensitive glass which is perhaps the most remarkable of all. If, for example, we use a substantial percentage of lithium in the glass we can precipitate lithium metasilicate as the white phase. Further work with this glass brought out the amazing fact that the opalized glass can be dissolved out by hydrofluoric acid so dilute that it is without appreciable action on the clear glass. That is, the glass dissolves only where the light has struck it. This gives us a new and revolutionary method of shaping glass (*4*). There are obviously many possible applications for this process where it is desired to reproduce a fine structure involving holes or grooves in glass. For example, fine glass screens up to 600 mesh may be made. Figure 5 shows a glass item made by this process.

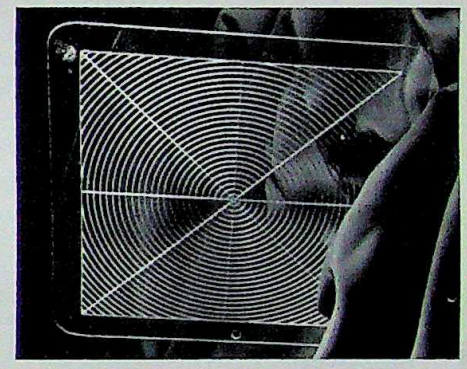


Figure 5. Item of chemically machined glass.

In pursuing the study of these chemically machinable glasses, Dr. Stookey found that they could, after proper exposure and sufficient heat treatment, almost completely be converted to a hard, fine grained, crystalline ceramic which has especially high strength. It was the study of such materials that ultimately led to the discovery of a whole new family of ceramics made from glass, the Pyroceram brand glass ceramics.

Up to this point in the story, the nuclei in these glasses had been produced by a photo process. However, nucleating agents, such as TiO_2, were found which could be incorporated in the glass batch and which would spontaneously precipitate out and form nuclei when the glass was properly heated. Following this nuclei-forming step the materials were heated at a higher temperature to produce crystal growth on these nuclei and to convert nearly all of the glass to a crystalline ceramic. The glasses that may be converted into ceramics by this process are not limited to one composition type but cover a field as broad as glass itself. In addition, for each glass composition we may obtain a number of different ceramics depending on the particular heat treatment used in the conversion. Thus the multiplicity of possibilities is almost endless.

The products obtained by this carefully controlled conversion of glass into a ceramic have many unusual

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and valuable properties (*5*). They have greater strength and greater surface hardness than glass. In general they will stand higher temperatures. Higher heat conductivities may be obtained. One of the remarkable features is the wide variety of possible expansions which range all the way from -50 to $+ 200 \times 10^{-7}$/°C. Electrical properties may also be varied widely. By growing extremely small crystals, these glass ceramics may even be made transparent.

Of the thousands of compositions so far studied, space permits specific mention of only the two that have been of most practical interest.[1]

The first to find commercial application was the glass-ceramic Code No. 9606 which is used for the radome of some missiles. Tables 4 and 5 list the properties of this material. The good electrical characteristics, high service temperature, high strength and low density were the principal factors favoring its choice for this application. Figure 6 is a picture of one of these radomes shown in both the glassy and the ceramic state.

[1] Since this was written, a third glass-ceramic has reached the commercial stage and is being used for the manufacture of a new line of dinnerware.

Table 4. Some Properties of Pyroceram No. 9606

Specific gravity (25°C)	2.60
Water absorption (°C)	0.00
Porosity	gas tight
Thermal expansion (/°C × 10^7)	57
Flexural strength (psi)	26,000
Hardness (Knoop − 500g)	618
Max. operating temperature (unloaded)	1000°C

Table 5. Dielectric Properties of Pyroceram No. 9606

25°C and 10^{10} cycles/sec.	
Dielectric constant	5.45
Dissipation factor	0.00033
Loss factor	0.002

Table 6. Some Properties of Pyroceram No. 9608

Specific gravity (25°C)	2.50
Water absorption (°C)	0.00
Porosity	gas tight
Thermal expansion (/°C × 10^7)	7
Modulus of rupture, psi	20,000
Hardness (Knoop)	588
Max. operating temperature	1000°C

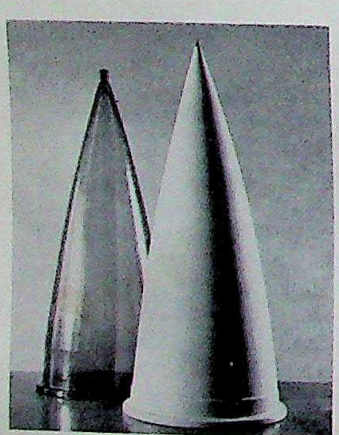


Figure 6. Radome of Pyroceram No. 9606 showing the original glassy state and the final piece after ceramming and finishing.

The other glass ceramic that I want to mention in particular is one that has enjoyed a very rapid rise to high volume production and I am sure that most of you have already seen it. I am referring to the glass ceramic Code No. 9608 which is used in Corning Ware cooking utensils and appliances. Table 6 lists the properties of this material. The outstanding characteristics are low expansion, high service temperature, high strength, and chemical inertness. It makes an ideal material for the handling and processing of foods. Figure 7 shows a skillet made of this material in its original glassy state and in the final ceramic state.

Strong Glass

The last part of this article will deal with the factors affecting glass strength and some of the recent developments in the way of strong glass.

The intrinsic strength of glass is surprisingly high. For example, measurements on fine glass fibers carefully prepared give breaking strength values ranging up to 1,000,000 psi. Calculations based on the energy of the Si-O bond predict these same high strength values and confirm that theoretically glass should be a very strong material—stronger in fact than steel. However, anyone who has ever dropped a milk bottle knows that there is something wrong with the theory. The discrepancy is due to the fact that the surface of glass develops flaws of various types which lead to stress concentrations. These flaws may be of appreciable size such as scratches, scuff marks, and scars that are easily visible, or they may be invisible microscopic defects that defy detection. If the glass is placed in tension the stress at the bottom of these flaws is greatly magnified and, since there is no give to the glass, a crack tends to propagate causing failure. If on the other hand the glass is placed in compression these minute flaws tend to close up and do no harm. This accounts for the well-known fact that glass is ordinarily very strong under compression but weak under tension and that a break invariably originates in a region under tension and usually at a point on the surface. This dependence of glass strength on the condition of the surface also accounts for the wide variations observed from sample to sample when a series of supposedly identical pieces are checked for strength. Such surface variations usually drown out the relatively minor effects of composition changes.

Table 7 gives a semiquantitative indication of the degree to which these flaws reduce the strength of glass. From the results it is apparent that our problem is not

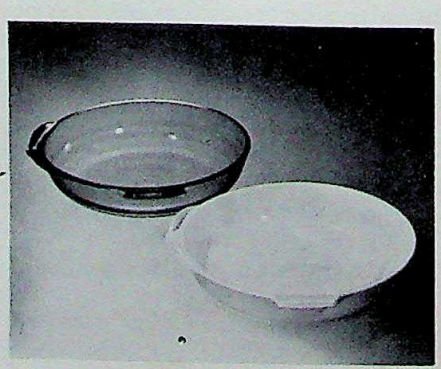


Figure 7. Skillet of Pyroceram No. 9608 showing the original glassy state and the final cerammed state.

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really to find a stronger glass than we have to find some way of preserving the high intrinsic strength with which the glass is originally endowed.

First, there are various ways in which we may protect the surface to avoid flaw formation. Of these, lubrication, surface coating and careful handling have been

Table 7. Typical Glass Strength Values

Ideal fiber—μ range	100,000 to 1,000,000 psi
Fine fibers—freshly drawn	30,000 to 400,000 psi
Drawn window glass	8,000 to 20,000 psi
Blown ware	5,000 to 10,000 psi
Pressed ware	3,000 to 8,000 psi
Abraded surfaces	2,000 to 6,000 psi
Deep file mark	500 to 1,500 psi
Average typical commercial item	5,000 psi

shown to be effective. The glass fiber-plastic coated ("armored") piping is an example of this approach as is also the use of coatings of a silicone or ammonium stearate. Through application of this principle we may achieve a worthwhile but not a striking gain.

Second, we may remove the surface flaws by fire polishing, mechanical polishing, or by dissolving away the surface glass with hydrofluoric acid. The latter method produces dramatic gains and breaking strengths up to 250,000 psi (on $^1/_4$ in. rods) have been obtained by this technique. However, the trouble with this approach is that the effect is only temporary since the flaws immediately start forming again. Application of a protective coating, such as a lacquer, will of course prolong the benefits of the treatment.

The third approach to the problem, which is by far the most important from a practical standpoint, is to put the surface under compression. A force which would normally produce tension in the surface will then merely neutralize part of the compression. The simplest method of doing this is by tempering the glass. This is accomplished by heating above the annealing point and then chilling rapidly. Thus, as the piece solidifies, the outside is at a substantially lower temperature than the interior. As the latter cools, it contracts and goes into tension thus putting the outside in compression. By this technique it is possible to realize a strength increase of 2 to 4-fold with ware of favorable dimensions. For an average piece this would mean a breaking strength in the range of 10,000 to 20,000 psi. This process has found practical application in a number of products including tumblers, industrial piping, windshields, etc. It suffers from the disadvantage that if the ware is heated to temperatures approaching the annealing range, the strength is lost.

Surface compression can also be achieved by providing a low expansion glass on the surface. On cooling from the annealing range the surface then contracts less than the interior with the result that it goes into compression. This type of compression has the advantage that it will not anneal out. The most obvious way of achieving this type of compression is by casing with a lower expansion glass. While this has been tried, it has not been used much commercially. Another method is by a high temperature ion exchange process in which the Na^+ in the surface layer is replaced by another univalent ion, for example Cu^+, Li^+, or H^+, which converts this layer to a lower expansion glass. Conversion of the surface glass into a lower expansion crystal layer offers another approach. A combination of the above principles has been utilized by Hood and Stookey (*6*). More recently, Kistler (*7*) has used a low temperature (below the annealing range) ion exchange process in which an ion in the surface glass, for example Na^+, is replaced by a larger one, for example K^+, thus putting the surface in compression.

However, the most recent and promising advance in the search for strong glass is that presented by Stookey, Olcott, *et al* (*8*), at the Sixth International Congress on Glass in Washington, D. C. (July, 1962). Two methods were disclosed. In one, the Na^+ in the glass surface is replaced by Li^+ in a high temperature ion exchange process and β-eucryptite crystals (very low expansion) are then grown in the surface layer. In the other process a glass is used which already contains lithium and the β-eucryptite crystals are formed in the surface layer by appropriate heat treatment. These methods have yielded strengths up to 100,000 psi in test specimens. What this means in performance is demonstrated by the fact that experimental glass cups made by the latter process have been dropped from the top of a nine-story building onto a steel plate without breakage. Thus, while we have still not attained the theoretical strength of which glass is capable, we have made a good start and our laboratory work indicates that we will soon reach the point where fragility ceases to be a limiting factor in the use of glass.

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American Science Manpower 1960

Over 200,000 US scientists are listed with the National Register of Scientific and Technical Personnel. 88% are employed full time in scientific work; 7% are women; 28% work for educational institutions; 31% have the PhD; 25% the MS. 23,000 of the 53,000 chemists are in organic. The complete report (NSF 62-43) is available for $0.65 from the US Government Printing Office, Washington 25, D. C.

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Chem Ed

BOOK REVIEWS

Gas Chromatography

D. Ambrose, National Chemical Laboratory, England, and *Barbara Ambrose*. D. Van Nostrand Co., Inc., Princeton, New Jersey, 1962. vi + 220 pp. Figs. and tables. 14.5 × 22 cm. $6.75.

Gas Chromatography

Ernst Bayer, Technological University, Karlsruhe, Germany. American Elsevier Publishing Co., New York, 1961. xii + 240 pp. Figs. and tables. 13.5 × 19 cm. Paperbound. $5.

Gas Chromatography

John H. Knox, University of Edinburgh, Scotland. John Wiley and Sons, Inc., New York, 1962. viii + 126 pp. Figs. and tables. 13 × 19 cm. $3.25.

Gas-Liquid Chromatography: Theory and Practice

Stephen Dal Nogare, E. I. du Pont de Nemours and Co., Inc., Wilmington, Delaware, and *Richard S. Juvet, Jr.*, University of Illinois, Urbana. Interscience Publishers (a division of John Wiley and Sons, Inc.,) New York, 1962. xviii + 450 pp. Figs. and Tables. 15.5 × 23.5 cm. $13.95.

The enormous growth of interest in gas chromatography in recent years is indicated by the nearly coincident appearance of these four books, by the more recent publication of another major book (Purnell), and by the first issue of an entirely new journal, *The Journal of Gas Chromatography*, to appear in January of 1963. To the specialist in the field the growth to such proportions in a single decade is exciting. To the general reader the attempt to follow the rapid development of the subject is usually frustrating. The books reported here should help considerably. It should be observed, however, despite the high stature of the authors, that no one individual can stay comprehensively abreast of the entire range of current developments in the field. This, coupled with the fact that a certain time is required for recent developments to gel into a unified picture, and that an additional time lag is encountered before the work is printed, means that one cannot expect a definitive treatise in such a fast-moving field. Within these limits the authors have done quite well, and have produced readable and informative books which present all but the most recent developments in the field of gas chromatography.

In order to better evaluate all four books for the general reader, this reviewer asked four students (three graduate, one undergraduate), whose past experience with gas chromatography ranged from practically zero on up to a full year, to read the books and comment on their relative usefulness. Without exception the Dal Nogare and Juvet book was ranked as most informative. This rating still held, for the most part, when comparing this more expensive volume on a dollar for dollar basis. As succinctly stated by one student, "The authors' methods of organization, the partial treatment of theoretical and experimental conditions, the detailed discussion of instrumental components, and the many useful laboratory data and tables, in my opinion make their book an essential volume." This reviewer agrees with the over-all high opinion of this book. In a field where the technique and the instrumental system can be varied in an unfathomable number of ways, it is imperative, if unity of treatment is to be achieved, to develop the experimental discussion by reference to the underlying principles. While all of the authors have tried this approach, only Dal Nogare and Juvet have really succeeded. Their theoretical discussion is the most complete yet published in book form, and the authors show great skill in bringing to light those factors which are really significant in determining the success of a given separation.

Each area is discussed, insofar as possible, by reference to these fundamental parameters. Despite this fundamental approach the book has a wealth of practical detail with chapters on the liquid phase, solid supports, the mobile phase, sample introduction, detectors, qualitative and quantitative analysis, capillary columns, high boiling compounds, trace analysis, programed temperature, preparative scale and special applications. The book is, on the whole, well written. The treatment is rather advanced, although the first four chapters present a more elementary survey of the field which allows the reader to acquaint himself gradually with the difficult concepts. The only real criticism of the book is that, despite its relative pre-eminence in presenting realistic theory, some concepts could be treated with more authenticity and less difficulty; e.g., the mathematics of the plate model (used also as an approach in the other books) is a difficult hurdle which is no longer necessary in presenting chromatographic theory.

For the reader who is not interested in such a lengthy and expensive treatise as that by Dal Nogare and Juvet, the problem is more serious. In fact none of the other books really presents a concise and valid survey of gas chromatography. Each book does, however, cover one or more particular areas in an excellent manner, and may therefore fulfill the needs of certain readers.

The consensus of the student reviewers was that the best short survey was written by Knox. There is no doubt that the style is fluid and the coverage is fairly broad. In principle the author's approach is very sound; an extensive (nearly one-fourth of this short book) treatment of the fundamental column theory is followed by experimental detail. Unfortunately the chapter on theory is far less satisfactory than the subsequent chapters. The mathematics of the plate theory, rapid analyses, etc., occupy space that should be allocated to answering the very fundamental questions of how and why the elementary physical processes in the column are leading to the observed zone profiles. The classical van Deemter equation is described and used, but practically nothing is said of how its various terms originate. The only valid reason

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Norbert A. J. Platzer, Polymerization and Polycondensation Processes: A Collection of Papers Based on the Symposium on Polymerization and Polycondensation Processes

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for sacrificing elementary concepts is to keep the treatment absolutely simple, but unfortunately this was not done.

The books by Ambrose and Ambrose and by Bayer are generally comparable, both in length and scope. Each presents a useful, but limited, theoretical discussion. These books delve into numerous practical details, but the treatments are not always carefully unified and integrated together. Neither book is as up-to-date as the one by Dal Nogare and Juvet; references since the end of 1959 are in a distinct minority. The book by Ambrose and Ambrose emphasizes the equipment of gas chromatography, and gives many excellent discussions which would aid the individual making his own apparatus. The monograph by Bayer emphasizes the methods of separation of particular classes of compounds, giving in many cases sufficient detail to help the investigator with a particular separatory problem. Along with these particular emphases, each book presents a fairly well balanced picture of the over-all technique.

Although its later publication precluded the formal survey of Purnell's book (John Wiley, 441 pages) in this review, a few comments should help align the book with respect to its precursors. The scope of this book is broad, it is quite well written, and its many practical applications are discussed in the light of recent theoretical developments. This book is comparable in most ways to the one by Dal Nogare and Juvet, and must therefore be rated as excellent.

J. Calvin Giddings
University of Utah
Salt Lake City

Biochemical Applications of Gas Chromatography

H. P. Burchfield, Southwest Research Institute, San Antonio, Texas, *Eleanor E. Storrs*, Boyce Thompson Institute, Yonkers, New York. Academic Press, Inc., New York, 1962. xviii + 680 pp. Figs. and tables. 16 × 23.5 cm. $22.

In this book the first 137 pages are devoted to general techniques, conventions, and instrumentation. The remainder is a laboratory manual dealing with specific uses of gas chromatography. Most of the methods were revised by the original authors. Generally, enough information is given so that a method may be reproduced in one's own laboratory, including directions for isolation and preparation of the sample.

In common with any text on gas chromatography, the book was somewhat out-of-date before it appeared. Because of this, there is very little discussion of temperature programing.

The book appears to be quite free of errors. However, the shorthand designation for branched chain fatty acid esters is given incorrectly on page 489. The discussion of peak broadening on page 4 is somewhat ambiguous. It is stated that slower-moving peaks give wider peaks, although according to the theoretical plate concept, peaks exhibiting the same number of theoretical plates have the same relative width (i.e., peak width divided by retention time).

Reference should have been made to Janak's work (*J. Chromatog.* **3**, 308, 1960) in the discussion on integration of peak areas. The discussion on column ovens did not make clear that there are three methods of heat control, namely variable transformer, thermostat, and electronic proportional control in order of complexity. An example of thermostat control was given although this is least desirable because of temperature cycling.

Only a few typographical errors were noted. The most noticeable was an incorrect initial for A. T. James in the author index.

The chapter on lipids was examined closely and was found to be very complete and well done.

The book is recommended for anyone who owns or is considering the acquisition of a gas chromatograph. It is hoped that revised editions can be issued at frequent intervals.

Lloyd A. Horrocks
Cleveland Psychiatric Institute
Cleveland, Ohio

Physical Aids to the Organic Chemist

M. St. C. Flett, ICI Ltd., Manchester, Great Britain. American Elsevier Publishing Co., Inc., New York, 1962. 388 pp. Figs. and tables. 13.5 × 19.5 cm. $8.

It is paradoxical that as physical methods of investigation become more and more important in organic chemical research, the education of organic chemists in physical chemistry is deteriorating. The difficulty is not primarily that organic chemists are uninterested in physical chemistry, but rather that graduate physical chemistry courses have become so fundamental, so much concerned with the principle of physics and so sophisticated in mathematical language, that they are no longer meaningful to most students of organic chemistry.

A different problem is that as new physical methods have been added, at intervals of perhaps four years, to the arsenal of the organic chemist, "know how" concerning their potentialities, limitations, and mode of operation has tended to accumulate more as laboratory lore than in systematic written form. Transmission of lore from one student generation to another being rather inefficient, valuable techniques or aspects of a technique once familiar in a laboratory may come to be neglected and forgotten.

In these circumstances, there is need for courses and books to teach organic chemists the theoretical principles upon which physical techniques are based and to discuss the application of these techniques to practical problems. The theoretical treatment need not give proofs or derivations, but it must present authoritatively if qualitatively those aspects of the theory which account for the main results observable by the organic chemist.

Flett's book is addressed to this need and satisfies it excellently.

Chapter titles indicate the subjects covered: Chromatographic Separation, Gas-Liquid Chromatography, Zone Refining, Electronic Absorption Spectroscopy, Infra-red Spectroscopy, Electron Spin Resonance Spectroscopy, Nuclear Spin Resonance Spectroscopy, Mass Spectrometry and X-Ray Crystallography.

To quote from the Preface: "Each chapter begins with a short description of the theoretical principles and experimental methods of a technique under discussion. The main emphasis throughout is, however, on the applicability of the various methods to organic chemistry, and most of the book is therefore devoted to examples of chemical applications."

The standard of the book is high, both in the writing and scientifically. The theoretical presentations are often crude in that they skip over subtleties to get quickly to the main point. But this abruptness finds its reward in the opportunity to go into special features of theory of much practical importance. With few exceptions, theoretical discussions are well done. Colleagues of mine expert in infrared and electron spin resonance spectroscopy raised no serious objections to those chapters.

Each chapter is concluded by a good bibliography of books and research and review papers. British publications tend to be cited more than American.

The book has a few faults. Thin layer chromatography escapes mention, the discussion of bonding in ethylene is badly done, and the book is poorly bound.

Flett's book is strongly recommended for individual purchase by every organic chemist and graduate student.

Joseph F. Bunnett
Brown University
Providence, Rhode Island

Encyclopaedic Dictionary of Physics. Volumes 2 to 6

J. Thewlis, editor-in-chief, Atomic Energy Research Establishment, Harwell, England. Pergamon Press, New York, 1962. Figs. and tables. 19.5 × 25.5 cm. $240 per set.

With the arrival of volumes 2 to 6 of the Encyclopaedic Dictionary of Physics it is possible to obtain a more comprehensive view of this enormous piece of work. The volumes range in topics for Volume 2 from "Compensator" to "Epicadmium Neutrons" in 880 pages, for Volume 3 from "Epitaxy" to "Intermediate Image" in 894 pages, for volume 4 from "Intermediate State" to "Neutron Resonance Level" in 836 pages, for Volume 5 from "Neutron Scattering" to "Radiation Constants" in 782 pages and for Volume 6 from "Radiation, Continuous" to "Stellar Luminosity" in 883 pages.

Whether the eight volumes can be considered to "span all current knowledge of Physics and related subjects" as the publisher's announcement states is a

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matter which each individual will have to decide for himself. Certainly the topics are covered in as extensive a manner as most readers would wish for. With the increase in physical knowledge this dictionary can save one a great amount of time in becoming acquainted with the phenomena covered. This is not to say that all the articles can be read by an interested reader without some prior knowledge, for those using extensive mathematics call for some prerequisite knowledge. Many of the articles on Quantum Mechanics use considerable mathematics, though the article on "Nuclear Forces" by Professor Breit of Yale University is largely descriptive and quotes the mathematical theory making no attempt to derive any of the equations. This latter article has a whole page of references! It would probably be an advantage to many readers had more of the articles followed the pattern used by Professor Breit.

As an example of the manner in which different aspects of a topic are treated, consider that of Electrochemistry. This begins with: "The academic definition refers to the study of the behavior and properties of electrolytes and ions in solution or in the fused state, whether or not electric currents are involved. The practical definition refers to the effects of passing electricity through electrolytes, e.g., electroplating, chemical decomposition, gas evolution, chemical analyses with electrical apparatus; and the generation of electricity by chemical means, i.e. batteries of all types." Altogether this topic takes up eighteen double column pages with a number of short articles ranging from a few lines to a few paragraphs as well as longer discussions of a page or more on Electrode, Electrodeposition, Electrode Potential, Electrokinetic Phenomena, Electrolysis and Electrolyte. At the end of all the longer articles and many of the shorter ones are references to a more complete literature, mainly books.

The heading Mathematics provides a short article on philosophical problems where it is stated "David Hilbert formulated the task of comprehending the whole of mathematics within a single axiomatic system and proving the consistency of this system by finitist methods of the greatest stringency. Gödel proved that this goal was unattainable. . . ." As André Weil said "God exists since Mathematics is consistent and the Devil exists since we cannot prove it." Following this are articles on the Mathieu Function, Matrices and Matrix Mechanics all of which use the technical side of mathematics.

A one page article on the Mössbauer Effect presents a brief but illuminating account of this phenomenon and shows how this has been used to test the principle of equivalence in general relativity.

It can be readily appreciated that these volumes present a most impressive piece of work by a host of able contributors. They will undoubtedly help the physical scientist as well as many others who make use of physical phenomena. While the price will prevent many individuals from owning their set of this Dictionary it should be readily available to all scientists. It is doubtful if there is any scientist who cannot find something of considerable use to him in the pages of this Dictionary.

R. J. Stephenson
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Basic Experimental Organic Chemistry

James Cason and *Henry Rapoport*, both of the University of California, Berkeley. Prentice-Hall, Inc., Englewood Cliffs, New Jersey, 1962. x + 273 pp. Figs. and tables. 15 × 23 cm. Paperbound. $3.75.

This volume, a paperback edition of Part I of "Laboratory Text in Organic Chemistry," second edition, by the same authors,[1] will be welcomed especially by the large numbers of students who take organic chemistry laboratory but are not chemistry majors—students who chafe at the necessity of buying a more expensive lab text which contains much material beyond the scope of their course. For the chemistry major however, the larger "Laboratory Text" is recommended as an excellent addition to his personal reference library. The paperback edition permits both kinds of students to have practical texts in the same course.

Teachers of experimental sciences have long defended the required undergraduate laboratory as the place where the lecture material is really learned. Numerous lab manuals have apparently been based on this dictum. Cason and Rapoport boldly declare however that the primary intent of their laboratory course is to teach laboratory operations: illustration of lecture material is strictly secondary. There is no effort to correlate the lab work with any particular approach (or text) in lecture, a wise choice which permits this lab text to accompany any lecture text. With greater and greater emphasis on the theoretical aspects in modern lecture texts for organic chemistry, a lab text which emphasizes the essential laboratory skills, without which few theories can develop, is welcome.

The kinds of experiments are not revolutionary; rather they are basic and well tested. Included are 4 chapters on techniques, 12 on transformations of simple functional groups, one on sugars, 6 on aromatic substitutions, 5 on heterocyclic syntheses, and one on qualitative organic procedures. The equipment specified includes some items with standard taper joints (eliminating nearly all stoppers and corks), although the directions allow the substitution of equipment without ground joints. The ground joint equipment called for is so cleverly chosen that the added cost per student is only about $15. The illustrations are excellent. The experiments do not utilize mechanical stirring, reduced pressure distillations or modern analytical instruments such as spectrophotometers and gas chromatographs.

In spite of the declared secondary importance of illustrating lecture material, Cason and Rapoport include considerably more lecture-type discussion than do most lab manual authors. Even so, the attention to the experimental aspects of the reactions discussed make this material supplementary to, rather than repetitious of the presentation most likely included in lectures.

This text is heartily recommended for use in the undergraduate organic chemistry laboratory requiring a text. I strongly endorse the primary emphasis on laboratory operations. The most serious criticism, perhaps the only one, suggested for this book is that it fails to communicate the excitement that organic chemists experience in the laboratory. Professor M. S. Newman's enthusiasm for new approaches to laboratory teaching for chemistry majors[2] is so infectious that this reviewer has become unsatisfied with available laboratory texts. Compared with what organic chemistry is really like, all lab manuals that I have examined seem dull. But perhaps the beginning student sees through different eyes, and nearly any experiment performed for the first time will be interesting. This is a time of active controversy about the most desirable organization and emphasis in organic chemistry lectures, with various new approaches being advocated.[2] It seems a pity that there are so few experiments with the experiments.

James G. Traynham
Louisiana State University
Baton Rouge

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[1] Reviewed by H. G. Kuivila in This Journal., **39**, 602 (1962).

[2] See, for example, the "Symposium on the Teaching of Elementary Organic Chemistry," Abstracts of ACS Meeting, September, 1962, pages 1–3F.

Laboratory Practice of Organic Chemistry

G. Ross Robertson and *Thomas L. Jacobs*, both of the University of California, Los Angeles. 4th ed. Macmillan Co., New York, 1962. ix + 383 pp. Figs. and tables. 16.5 × 24.5 cm. $5.50

Since the current edition of this fine laboratory manual exhibits improved presentations of its several commendable features, this reviewer's impression of it is just as favorable as was that of the previous edition (This Journal, **32**, 340 [1955]).

Although the general format of the book is essentially unchanged, several rearrangements have been made, especially in Part I (Theory and General Technique, 163 pp.). Some obvious changes in Part I are: Chapter 4 (Conduct of the Reaction, 12 pp.) contains the revised material of Chapter 3 (Temperature Control) of the previous edition; Chapter 5 (Distillation-Single Liquid Substances, 30 pp.) has discussions of solutions and the principles involved in the various types of distillations, hence it is a revision of the material

(*Continued on page A142*)

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New AP Publications

Physical Methods in Heterocyclic Chemistry

Edited by A. R. KATRITZKY, *Cambridge, England*

Volume 1—NONSPECTROSCOPIC METHODS
January 1963, 346 pp., $12.00

Volume 2—SPECTROSCOPIC METHODS
Spring 1963, about 400 pp.

Physical Methods in Heterocyclic Chemistry concentrates in one convenient work reliable guides to the physical methods useful in heterocyclic chemistry. The coverage is extensive and the treatment detailed—numerous tables and references are included.

This treatise is directed to the organic chemist, enabling him to make advantageous use of the new techniques available. In this respect the volumes will be invaluable for their concentration of information heretofore scattered in many different publications.

Adsorption and Collective Paramagnetism

By P. W. SELWOOD, *University of California, Santa Barbara*

October 1962, 189 pp., $7.50

This research monograph describes a novel method for studying molecular interactions on solid surfaces through measurements of magnetization. The method is applicable to solids exhibiting collective paramagnetism (superparamagnetism), and is based on work in the author's laboratory. Chief applications are to the mechanism of chemisorption, to heterogeneous catalysis, and to related surface phenomena, with certain implications concerning the magnetic properties of transition elements and their compounds.

Study Manual in Physical Chemistry

By F. E. CONDON, *The City College of New York*
March 1963, in preparation

This unique study manual consists of exercises based on experimental data from the original literature. It is not a book of problems in the usual sense. Rather, the student is given a set of data and guided in its application to the solution of specific problems or the determination of constants. This new approach to teaching exposes the student to results actually obtained in the laboratory and provides him with practice in the application of principles presented in the classroom to these results.

Examination copies for classroom adoption are available upon request.

Colloidal Surfactants

Some physicochemical properties

By K. SHINODA, *Yokohama National University*
T. NAKAGAWA, *Shionogi Pharmaceutical Company*
B. TAMAMUSHI, *Tokyo Women's Christian College*
T. ISEMURA, *Osaka University*
November 1962, 312 pp., $11.50

The use of surface active agents in many areas of the chemical industry and their interest to scientists in various fields has brought about rapid progress in research concerning these substances. In this book the authors give a complete and up-to-data survey of current knowledge of the fundamental processes involved as well as a comprehensive discussion of applications.

This work will be of interest to all workers engaged in research or applications concerned with surface active agents in chemistry, biochemistry, biology, or medicine. It contains many results and concepts either previously unpublished or published only in Japanese. No other book gives such complete coverage of the solution of purified nonionic agents.

New Serial Publications

Science of Ceramics

Proceedings of a Conference held at Oxford under the auspices of the British Ceramic Society and the Nederlandse Keramische Vereniging

Edited by by G. H. STEWART, *The British Ceramic Society*

Volume 1, December 1962, 334 pp. $11.50

This volume deals with topics having an important bearing on the development of ceramics, such as the methods of determining the structure of clay, the relationship of clay minerals, sintering, plasticity, the study of pore-size distribution, mechanism leading to fracture, compositions having a dielectric constant of 10,000 at room temperature, barium titanate, fluoride ceramics, and the physical properties of crystal-glass ceramics. The book will appeal to a wide readership whose interests extend from clay to the properties of fired bodies. The investigation work reported embraces problems that connect porcelain on the one hand with special ceramics for the production of atomic energy and electronics on the other.

Residue Reviews

Residues of Pesticides and Other Foreign Chemicals in Foods and Feeds

Edited by FRANCIS A. GUNTHER, *Citrus Experiment Station, University of California, Riverside*

Volume 1, November 1962, 162 pp., $6.50
Volume 2, Spring 1963, about 160 pp., $6.50

The purpose of "Residue Reviews" is to provide concise, critical reviews of timely advances, and to outline significant areas of accomplished or needed endeavor in the entire field of residues of these chemicals in foods, in feeds, and in transformed food products. These reviews encompass analytical chemistry and its methodology, biochemistry, human and animal medicine, legislation, pharmacology, physiology, regulation, and toxicology; certain aspects in the realm of food technology that are concerned specifically with pesticide and other food-additive problems are also scheduled for coverage.

Contributions are published in English, French, or German.

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previously in Chapters 5, 7, 8 and 9. Chapter 6 (14 pp.) describes the techniques of distillations; Chapter 7 (Behavior of Solid Substances, 16 pp.) has revised material formerly in Chapters 14 and 15; Chapter 8 (Techniques of Preparation of Solids, 16 pp.) has topics previously in Chapters 12 and 13; Chapter 11 (Solubility of Organic Compounds, 10 pp.) now follows the discussion of extraction, adsorption and chromatography in current Chapter 9 (16 pp.); Chapter 14 (The Literature of Organic Chemistry, 8 pp.) is longer and better than its earlier counterpart; Chapter 15 (Writing of a Research Report) is comparable to Experiment 56 (Library Problem) of the previous edition.

The revision of Part II (Laboratory Experiments) seems to be less extensive than that of Part I, although many changes have been made. Notable additions to Part II are Experiments 8 and 44 on chromatography. In Experiment 44 is a list of 18 dyes approved for use in foods, drugs and cosmetics. Experiments deleted from Part II are alcohol by fermentation, derivatives of nitroparaffins (except acetoxime) and preparations of crystal violet and *n*-butylbenzene. The section on qualitative organic analysis has been improved by expansion. Although the section on literature references to special preparative experiments is similar to its predecessor, some interesting additions are preparations of triallylamine, *n*-hexyl fluoride, 7-anthraldehyde, 2,4,6-tri-*tert*-butylphenol, 2-iodothiophene, ferrocene and *n*-butyllithium.

Because this manual has so many assets, it merits the attention of everyone who is interested in the teaching of organic chemistry in the laboratory.

Donald C. Gregg
University of Vermont
Burlington

Theory of Molecular Excitons

A. S. Davydov. Translated by *Michael Kasha,* Florida State University, Tallahasee, and *Max Oppenheimer, Jr.,* State University of Iowa, Ames. McGraw-Hill Book Co., Inc., 1962. ix + 174 pp. Figs. and tables. 16 × 23.5 cm. $7.95.

The translation by Kasha and Oppenheimer of Professor Davydov's fairly old Russian book is an extremely welcome addition to the English speaking literature. The book represents the treatment of Davydov's contribution to the theory of molecular spectra, in particular, his approach to treating molecular spectra as excitons. This is a very useful concept, not only in the field of the spectra of solids, but in many related fields which involve the transmission of excitation from one site to another in a solid. Unfortunately, the fact that the vast majority of the literature concerning this area is in Russian has had the effect that it is little understood, and little used in the English speaking world. The availability of the translation of Professor Davydov's work should do much to overcome this difficulty.

The book is not easy to read. It is a highly mathematical treatment, and many practicing chemists will find it far beyond their comprehension. It is addressed to the specialist; it is understandable really only to him. One can certainly not recommend it to the average chemist for rapid reading or scanning, although, the theoretical physical chemist with interests in spectroscopy will probably find it a must.

The usefulness of the book is greatly enhanced by two appended bibliographies: 1, the papers of Davydov's following the publication of the book, containing some 57 entries, and 2, a bibliography of publications on excitons, mostly from the western world, with about forty entries. The book is well made, attractively bound and, for the very small market, does not appear excessively expensive.

H. H. Jaffe
University of Cincinnati
Cincinnati, Ohio

Absorption Spectra and Chemical Bonding in Complexes

C. K. Jørgensen, Cyanamid European Research Institute, Cologny, Geneva, Switzerland. Addison-Wesley Publishing Co., Inc., Reading, Mass., 1962. xii + 352 pp. Figs. and tables. 14.5 × 22.5 cm. $10.

We now know how to interpret at least the gross features of the absorption spectra of complexes of the transition metal ions. Furthermore, while the study of these spectra has usually been aimed at clarifying the electronic structures of the several metal ions, a parallel reward has often been an insight into the nature of the various ligands. This book attempts to survey these areas of inorganic chemistry with the ultimate aim of summarizing current ideas on the nature of the chemical bond in complexes.

The author is only partially successful, however. The book could certainly not be an introduction to the field for the untutored; it is far too concerned with controversies to be a useful textbook. Yet, it is not clear for whom the book was designed. Thus, the first chapter is a historical introduction not only to bonding in complexes, but to the bonding in all chemicals. The second chapter follows with a discussion of the application of density matrices! Certainly this is an uneven level of sophistication, characteristic of much of the book.

Jørgensen summarizes much of the available data and discusses and criticizes the various theories and interpretations of spectra and the factors which affect them. Thus, chapters are devoted to each of the topics: molecular orbitals, spectrochemical series, nephelauxetic series, electron transfer spectra, and so on.

The book is an excellent reference for the specialist in the field, for some 950 references are listed, along with a large number of spectral results and electronic parameters included in some 34 tables and 29 diagrams. Further, Jørgensen is prolific and highly original in his interesting suggestions for new research.

A chapter discussing the methods of determining stability constants in solution is included as is also a discussion of the solution chemistry of the metal ions; these chapters seem out of place here.

All in all, this book will be of use to the worker in the field as a reference, but of rather limited general appeal.

Richard L. Carlin
Brown University
Providence Rhode Island

Direct Analysis of Diffraction by Matter

R. Hosemann, Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin, and *S. N. Bagchi,* University of Calcutta, India. North-Holland Publishing Co., Amsterdam, 1962 (distributed in U.S. by Interscience Publishers, Inc., New York). xxi + 734 pp. Figs. and tables. 16 × 23 cm. $21.75.

This book is concerned with the problem of deriving the atomic arrangement in matter by *direct* interpretation of information obtained through the diffraction of X-rays, electrons, or neutrons.

Direct methods, as opposed to trial-and-error methods and other indirect procedures requiring the application of human ingenuity and judgment, have long been sought after by X-ray crystallographers, but except in certain favorable cases the end of the search is not in sight. In X-ray crystallography the atomic arrangement is often found by use of the Patterson function, which is calculated by means of a Fourier series in which the squares of the diffraction amplitudes appear as coefficients, no knowledge of the phases of the diffracted waves (which are inaccessible to direct experiment) being required. The Patterson function is the "folding" or "convolution product" of the electron density function, and the latter is a "folding root" of the Patterson function, obtained by some "deconvolution" procedure. In general there exist an infinite or quasi-infinite number of folding roots of a given Patterson function; to obtain a unique root it is necessary to introduce restrictions on the numbers and shapes of the atoms present, based on chemical and physical knowledge. This amounts to treating the Patterson function as being composed of a finite number of characteristic peaks, each corresponding to the interatomic vector between two atoms.

Erratum:

With Mark Twain, C. W. Wood can say that the report of his death was greatly exaggerated. Mr. Wood, identified in a book review caption of the November Journal (page A906) as "deceased" is very much alive. We regret any embarrassment we may have caused him or his family.

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An Introduction to the Use of Mathematics in Chemistry

By Sidney W. Benson, *University of Southern California.* The conversion factor approach to chemical calculations in this book has been extraordinarily successful in practice. It really succeeds in making the computational aspects of chemistry secondary to the physical content of the concept and ideas of chemistry. The second edition contains more problems, including many of greater difficulty, completely reworked sections on ionization and poly-electrolytes, and new tables summarizing descriptive properties and simple general rules for predicting products of chemical reactions. *1963. Approx. 256 pages. Prob. $2.95.*

CONFIGURATIONAL STATISTICS OF POLYMERIC CHAINS

By M. V. Volkenstein, *Institute of Macromolecular Chemistry, Leningrad. Translated from the Russian by* S. Timasheff. *An Interscience Book. 1963. Approx. 608 pages. $20.00.*

ION EXCHANGE SEPARATIONS IN ANALYTICAL CHEMISTRY

By Olof Samuelson, *Chalmers University of Technology, Goteborg, Sweden.* This revised and expanded version of the author's earlier book introduces new principles and refined techniques that are now recognized as valuable in practical analytical work. *1963. Approx. 450 pages. Prob. $12.00.*

NEW CHEMICAL ENGINEERING SEPARATION TECHNIQUES

Edited by Herbert M. Schoen, *Quantum, Incorporated.* Interscience Library of Chemical Engineering and Processing—Volume I. *1963. Approx. 448 pages. $14.50.*

MASS TRANSFER PROCESS CALCULATIONS

By H. Sawistowski *and* W. Smith, *both of the Imperial College of Science and Technology, London.* Interscience Library of Chemical Engineering and Processing—Volume II. *1963. Approx. 532 pages. $13.50.*

ORGANIC ELECTRONIC SPECTRAL DATA

A Comprehensive Catalog of Ultraviolet and Visible Spectra—Volume IV

Published under the auspices of the Organic Electronic Spectral Data, Inc. *Edited by* R. C. Nachod *and* J. P. Phillips. An Interscience Book. *1963. In press.*

INFRARED SPECTRA OF INORGANIC AND COORDINATION COMPOUNDS

By Kazuo Nakamoto, *Illinois Institute of Technology.* Covers the fundamental theory of molecular vibrations and features an extensive compilation of references. *1963. Approx. 320 pages. Prob. $9.50.*

OUTLINES OF BIOCHEMISTRY

By E. E. Conn *and* P. K. Stumpf, *University of California, Davis.* Using the most recent information, this book introduces biochemistry by treating reactions in terms of modern organic chemistry and emphasizing the electronic aspects of biochemical reactions. *1963. Approx. 416 pages. Prob. $8.75.*

QUANTITATIVE INORGANIC ANALYSIS

By Kazunobu Kodama, *Nagoya Municipal Industrial Research Institute, Japan.* An Interscience Book. *1963. Approx. 551 pages. Prob. $22.50.*

ORGANIC SYNTHESES—Collective Volume IV

Edited by Norman Rabjohn, *University of Missouri.* Contains the syntheses found in volumes 30 to 39 of the Organic Syntheses series. *1963. In press.*

ORGANIC SYNTHESES—Volume 42

An Annual Publication of Satisfactory Methods for the Preparation of Organic Chemicals.

Edited by Virgil Boekelheide, *University of Oregon. 1962. 118 pages. $4.25.*

EXPERIMENTS IN GENERAL ORGANIC AND BIOLOGICAL CHEMISTRY

By John R. Holum, *Augsburg College.* Offers experiments to supplement the author's *Elements of General and Biological Chemistry. 1963. Approx. 112 pages. $2.95.*

ADVANCES IN PETROLEUM CHEMISTRY AND REFINING

Edited by Kenneth A. Kobe, *and* John J. McKetta, Jr., *both of the University of Texas.* Interscience Books. Vol. 7: *1963 Approx. 530 pages. Prob. $21.00.* Coming soon: Vol. 8: *1963. In press.*

ADVANCES IN ORGANIC CHEMISTRY: Methods and Results

Edited by R. A. Raphael, *The University, Glasgow;* E. C. Taylor, *Princeton University; and* Hans Wynberg, *University of Groningen, Holland.* Interscience Books. Volume 3: *1963. 425 pages. $13.57.* Volume 4: *1963. Approx. 400 pages. Prob. $14.00.*

Kirk-Othmer: ENCYCLOPEDIA OF CHEMICAL TECHNOLOGY

Second Edition—Volume 1

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CHEMICAL INSTRUMENTATION

By Howard A. Strobel, *Duke University*

This book results from the author's experience as teacher of a one-year course for advanced undergraduate or one-year graduate students. Essentially a textbook, not detailing specific instrumentation techniques, the book provides a number of well-chosen problems and exercises.

653 pp, 373 illus, 1960–$10.75

INTRODUCTION TO STATISTICAL THERMODYNAMICS

By Terrell L. Hill, *University of Oregon*

"It is strongly recommended to chemists who are prepared to invest enough work to be able to understand what they are doing, and to physicists who seek a wider picture of the problems of statistical mechanics." (Physics Today)

"Treats the fundamentals adequately and the applications superbly." (Journal of the American Chemical Society)

508 pp, 97 illus, 1960–$10.75

INTRODUCTION TO THEORETICAL PHYSICAL CHEMISTRY

By Sidney Golden, *Brandeis University*

"This book is an attempt to present in a single volume the necessary background in theoretical physics for physical chemists. Although the book is elementary, it is quite rigorous." (Mathematical Reviews)

307 pp, 1961–$9.75

PHYSICAL GEOCHEMISTRY

By F. G. Smith, *University of Toronto*

The book includes material normally found only in scattered references; is designed for economic geologists, petrographers and mineralogists. Covers geochemical problems relating to melting and crystallization of rocks.

640 pp, 200 illus, 1963–$15.00

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BOOK REVIEWS

Finding the structure may in principle be accomplished through geometrical constructions that depend on necessary relations among interatomic vectors; this is often possible in practice if the structure is not too complicated. However there is no unique and infallible direct procedure for doing it, in the face of difficulties resulting from the limited range of diffraction data, frequent lack of resolution of Patterson peaks, etc.

In this book convolutions, deconvolution procedures, and the associated function algebra are treated and applied to analysis of diffraction not only by "ideal" crystals (which usually the X-ray crystallographer tacitly assumes his crystals to be) but also by real crystals possessing such nonidealities as finite size, various kinds of disorder, and atomic thermal motion. Even non-crystalline matter is treated. The central problem of the book is the deconvolution of the "Q function," which is a generalization of the Patterson function. (For a real bounded crystal, the Q function differs from the Patterson function in taking into account the fine structure of the diffraction maxima, including minute shifts away from reciprocal lattice points in certain instances.) In certain cases treated by the book the folding root of the Q function is unique (without additional assumptions), and there exist direct deconvolution procedures. It is a thesis of the book that this is true at least in large part for certain types of bounded crystals, provided that sufficiently detailed and precise measurements can be made of the intensity function in the diffraction pattern. It is largely on this basis that the book claims to present direct methods of structure analysis. Unfortunately, although some kinds of matter may fit such cases in principle they do not often in practice, and while the direct deconvolution procedures presented in the book are interesting and ingenious their effectiveness is largely undemonstrated except for very simple or hypothetical structures.

Thus, the book is less valuable for its methodology than for its exposition and development of principles in a manner and to an extent probably not found in any other single book in this area. Besides the convolution algebra and its applications as already mentioned, the book devotes a considerable amount of space to the fundamentals of "diffraction microscopy," many aspects of diffraction by crystals and paracrystals, small angle scattering, Compton scattering, scattering by fluids, and other topics. The high degree of specialization and the advanced mathematical level of the book will restrict its value to those actively working on diffraction problems. However, anyone having any acquaintance with diffraction phenomena will enjoy the many beautiful plates illustrating optical diffraction produced by various types of ordered and disordered two-dimensional patterns.

David P. Shoemaker
Massachusetts Institute of Technology
Cambridge

Continued on page a146

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☐ **MASS SPECTROMETRY:**
Applications to Organic Chemistry

By KLAUS BIEMANN, Massachusetts Institute of Technology. McGraw-Hill Series in Advanced Chemistry. 384 pages, $13.75.

Summarizes recent developments in the use of mass spectra of relatively complex molecules in research in organic chemistry, particularly for the determination of structure. It deals briefly with instrumentation and then discusses in detail the experimental techniques involved in obtaining a useful spectra of even relatively complex molecules. Emphasis is on a thorough discussion of mass spectra interpretation and of the fragmentation processes which produce such a spectrum.

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BOOK REVIEWS

Catalysis by Metals

G. C. Bond, The University, Hull, England. Academic Press, Inc., New York, 1962. ix + 519 pp. Figs. and tables. 16 × 23.5 cm. $15.50.

The author states that his reasons for preparing this book are two-fold. "First, the subject of catalysis by metals is one which, because it cuts across the conventional divisions of chemistry, has a diffuseness and incoherence which requires to be remedied. Second, this subject has reached a stage of advancement which makes an extensive review seem worthwhile." In his attempt to do this the author has carefully chosen the subject matter to avoid unnecessary detail. He aims to present information which establishes broad patterns and principles. This book should be useful to those engaged in catalytic research as well as to those who wish to become informed about this particular area of catalysis. It is not intended to be a text book.

The physics and chemistry of metals is briefly reviewed under the headings of characteristic properties of metals, geometric and electronic properties, electron band and valence bond theories of metals and properties of alloys. The next chapter considers the preparation or forming of metals as catalysts; the different microscopic forms of the pure metallic, supported, promoted and dual-function catalysts are discussed. Chapters 4–6 are on chemisorption in which the types, experimental methods, chemistry and energetics, and the kinetics of adsorption and desorption are very well reviewed. The chapter, The Kinetics of Surface Reactions, includes a discussion of the usual rate expressions and kinetic effects. Thus, the first 147 pages summarize the subject of catalysis on metals in general terms and provide excellent lists of references. Except for the final chapter, the author devotes the rest of the book to applications.

Chapters 8–19 (298 pp.) consider those systems where hydrogen and deuterium take part in the reactions, and have been organized into the general areas of isotopic exchange reactions, catalytic hydrogenation, Fischer-Tropsch synthesis, ammonia synthesis, hydrogenolysis, dehydrogenation and reforming. Again each chapter has an extensive list of references which include some for 1961. The coverage in these chapters is very good and the author has arranged the various subjects in an orderly and logical way. This reviewer questions the advisability of including the chapter on the Fischer-Tropsch synthesis. In the case of the iron catalyst under synthesis conditions the bulk phase consists of magnetite, Hägg-iron carbide and under certain conditions a carbide reported by Adcock and Eckstrom; alpha-iron is present only under rather unusual conditions. In the case of cobalt, again the bulk phase is the carbide rather than the free metal. Since this book is a review of metal catalysts, there would appear to

(*Continued on page A148*)

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Published March 1963 approx. 912 pages Text price: $7.95

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Walter J. Moore, INDIANA UNIVERSITY

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Published 1962 844 pages Text price: $13.00

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William T. Simpson, UNIVERSITY OF WASHINGTON

The valence bond and molecular orbital methods have for a long time been the backbone of attempts to understand the electronic structure of molecules. In this book, these methods are introduced and explained from a modern point of view and with an attempt at continuity and logical consistency. The independent system approach, which is useful for molecular crystals and certain molecules, is taken up in a similar way, and related to the time-honored other approaches. IN THE PRENTICE-HALL SERIES on CHEMISTRY. Also in the INTERNATIONAL SERIES on CHEMISTRY.

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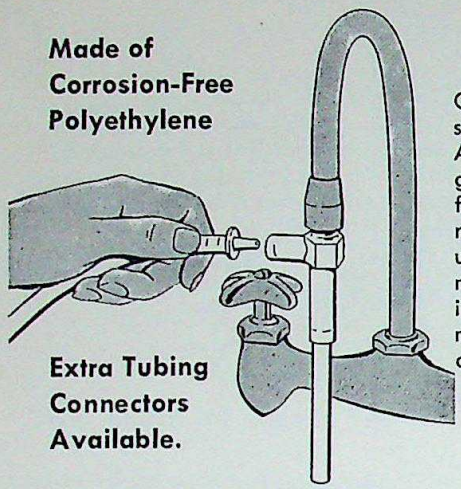
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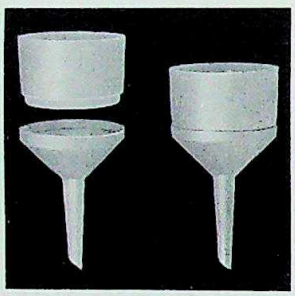
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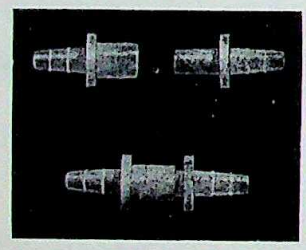
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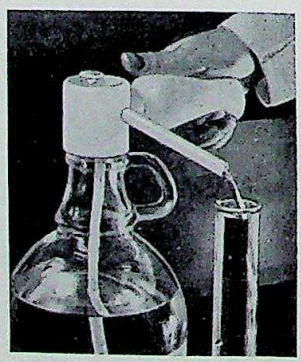
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BOOK REVIEWS

be no more reason to include the above catalytic process than those using a metal oxide catalyst. However, this is not a serious criticism except for the implication that the bulk catalyst phases are the free metal which is not correct in the case of iron and cobalt. Chapter 20 is entitled Catalytic Oxidation and includes catalytic oxidation of hydrogen, hydrocarbons, ammonia, carbon monoxide, sulfur dioxide, methanol, and the synthesis of hydrogen cyanide.

In the final chapter, Catalysis and Chemistry, the author reviews the preceeding chapters in an attempt to determine how the catalytic action of a metal depends on its geometric and electronic properties. He has posed the question "Is there any central and fundamental theme which may in the future give to the whole phenomenon of catalysis by metals a structure and coherence which it now lacks?" In this chapter, he reviews the material which bears on this "sought-for central theme."

There may be criticisms of this book, but the reviewer believes that the author has done an excellent job in separating "facts" from "theories" and in the assembly and condensation of a large amount of scientific information. This should be a valuable reference book.

HARTLEY C. ECKSTROM
University of Kentucky
Lexington

The Manufacture and Use of Fluorine and its Compounds

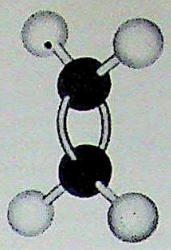
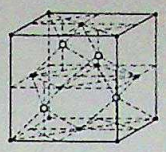
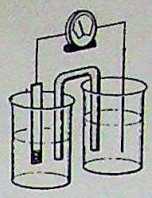
A. J. Rudge. Oxford University Press, London, 1962. xiii + 87 pp. Figs. and tables. 14.5 × 22.5 cm. $1.70.

Imperial Chemical Industries, Ltd. are to be congratulated upon this latest addition to a series published under their auspices which gives "short accounts of some aspect of industrial chemistry in order to make clear the relationship between the chemistry learned in school and the same chemistry as applied in industrial practice." The assistance rendered by two British science teachers' associations is reflected in frequent asides, footnotes, and one appendix, defining or explaining basic concepts needed in the text, such as hydrogen bonding, electrode polarization, wetting, and others. There is a determined and commendable effort to relate industrial problems, and their solutions, to the fundamentals of physics and chemistry. What students may be expected to know evidently differs on both sides of the Atlantic: American freshmen know what a hydrogen bond is; but few of them will appreciate the moving words of two pioneers of fluorine chemistry, Louyet and Moissan, quoted in the original French. Application of the principles of diffusion, *à propos* of UF_6, and of the temperature effect on chemical equilibria, *à propos* of ClF_3, would also have seemed appropriate to U.S. students; perhaps they are not to their British counterparts, for they have been slighted.

(*Continued on page A150*)

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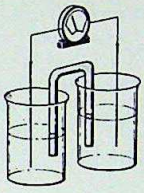
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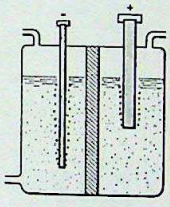

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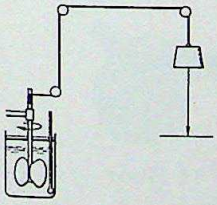


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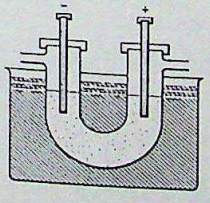


Pre-publication reviewers have been impressed with the organizational approach of GENERAL CHEMISTRY for the following reasons:

- Non-metal and metal chemistries are treated as units, rather than by families.
- Chapters are organized to permit maximum fit with laboratory work in the early part of the year. (Chemical calculations; reactions of gases, atomic weights, and solutions are introduced early in the text.)
- Many challenging problems are presented, though more routine problems are included. Answers worked out in detail in the Appendix help the fast student to concentrate on the more difficult problems and check his work as he goes along.



The following 24 chapter headings comprise the text: *Matter and Energy; The Particles of Matter; The Gaseous State; Chemical Calculations; Atoms; The Electronic Structure of Atoms; Valence I The Ionic Bond; Valence II The Covalent Bond; The Chemistry of Non-Metallic Elements I; Solutions; Electrochemistry; Acids and Bases; Introduction to Thermodynamics—The First Law; Thermochemistry; The Second Law of Thermodynamics; Chemical Kinetics; Chemical Equilibrium I. Principles; Chemical Equilibrium II. Applications; Electric Cells; Chemistry of the Non-Metallic Elements Part II; Chemistry of the Metallic Elements, Part I; Chemistry of the Metallic Elements, Part II; Organic and Biochemistry; Nuclear and Radiochemistry; Appendix.*



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BOOK REVIEWS

The major sections of the book deal with the manufacture, properties, and uses of hydrofluoric acid (9 pp.), fluorine (27 pp.), inorganic fluorine compounds (11 pp.), and organic fluorine compounds (21 pp.). Only compounds of actual or probable commercial importance are included. Some historic background is woven into the introduction and into the first two main sections; it is summarized in a chronological table. The emphasis is, of course, on industrial processes, though laboratory methods are mentioned. The author is an expert on British industrial fluorine chemistry; he frankly disclaims intimate knowledge of U.S. practices, but nevertheless deprecates them more often than seems necessary.

The writing is clear and concise. In a book of this scope, omissions are inevitable and constitute no grounds for criticism; the critical bibliography will lead the thirsty to deeper sources. A weakness is the industrial chemist's characteristically careless handling of nomenclature: oxygen fluoride, correctly named on p. 43, returns as "fluorine monoxide" on p. 44, and the formula is given as F_2O, rather than OF_2, in both instances; compounds of the type $C_xH_yF_z$ are called "fluorohydrocarbons" on p. 58 and, less sensibly, "hydrofluorocarbons" on p. 67; analogously, one would prefer "chlorofluorohydrocarbons" to "hydrochlorofluorocarbons" (p. 58); the numerical prefix "quindeca-" for pentadeca- (p. 76) is sanctioned neither by philology nor by IUPAC.

The book is very well produced. Tables, figures, and plates are used effectively. This reviewer found only one typographical error, on p. 32, where a contact angle is given as "140° C." There is no subject index; but this short book is meant for reading, not for reference.

The quality and brevity of the book recommend it as required reading for students of chemistry and chemical engineering, if not in the freshmen year, then in advanced inorganic or industrial chemistry courses. Its price leaves no excuse for any college library to be without it.

CURT W. BECK
Vassar College
Poughkeepsie, N.Y.

Scientific Russian

A. Holt, College of Advanced Technology, Birmingham, England. John Wiley & Sons, Inc., New York, 1962. xv + 195 pp. 14.5 × 22 cm. $6.25

This book is intended as an introductory course in grammar and reading; it consists of two parts.

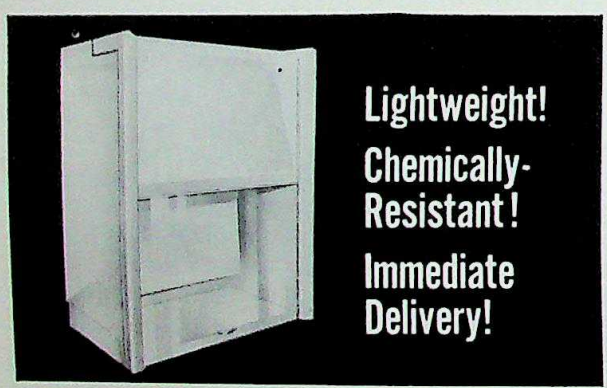
Part I (pp. 1—78) consists of 22 lessons arranged in the following format: vocabulary, extremely brief discussion of pertinent grammar, and an exercise for reading and translation. According to the vocabulary of Part I, the title of the book is a misnomer; it should be "Chemical Russian." Although accent marks are provided in each exercise, where they are not important, they are omitted from the individual vocabulary and the excellent glossary (pp. 161–194) where they really belong.

Part II (pp. 79—106), entitled Grammatical Summary, includes the subjects of transliteration, chemical nomenclature, and a condensed presentation of Russian grammar. The translation exercises (pp. 107—160) deal with a more varied scientific repertoire; of the 37 exercises, 15 are concerned with chemistry, 12 with biology, and 10 with physics; none are from current research journals.

The book is well printed, adequately covered, and free of errors. It is a good introductory book for a student chemist; the author is a Russian-reading practising chemist who knows precisely what is necessary, and what can be omitted, if the student's only goal is to be able to read Russian technical material. The book is well organized but suffers from some general deficiencies discussed previously in THIS JOURNAL, **37**, 162(1960); **38**, A500(1961).

IRVING S. BENGELSDORF
U. S. Borax Research Corporation
Anaheim, California

(*Continued on page A152*)



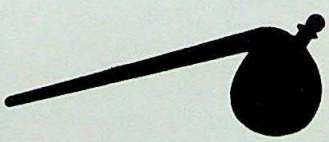
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BOOK REVIEWS

Substitution at Elements other Than Carbon

C. K. Ingold, University College, London. 5th Weizmann Memorial Lecture Series, 1958. Weizmann Science Press of Israel, 1959. Available in the U. S. from Interscience Publishers, Inc., New York. 52 pp. Figs. and tables. 14.5 × 22 cm. $3.50.

This book contains two chapters which summarize 4 lectures delivered by C. K. Ingold on the occasion of the 5th Weizmann Memorial Lecture Series, May, 1958. The first is entitled Nucleophilic Substitution at Octahedral Metal Atoms, in Particular Cobalt and the second Electrophilic Substitution at Nitrogen and Oxygen.

The discussion in chapter I is based on the premise that the more complicated mechanisms of substitution of ligands of complex ions are best understood when compared with the simpler nucleophilic substitutions at carbon. The lecturer develops an interpretation based on available rate and stereochemical data which he characterizes thus: "I do not dare to hope that the interpretations I have suggested are correct in their entirety. But I do believe them sufficiently to think they are more likely to be modified than scrapped."

In Chapter II the lecturer deals with [illegible] in his usual thorough manner. First he indicates the possible species that can be the reagent and shows the kinetic form that the rate equation should have for each. Comparison of the experimental results with the kinetic forms expected gives strong indications as to the nature of the reactive species under different conditions. This chapter gives a convenient summary of the mechanism of nitration and nitrosation.

This short book is worthy of inclusion in a chemists' personal library.

John D. Reinheimer
The College of Wooster
Wooster, Ohio

Polymerization and Polycondensation Processes: A Collection of Papers Based on the Symposium on Polymerization and Polycondensation Processes

Norbert A. J. Platzer, Monsanto Chemical Co., Springfield, Massachusetts, symposium chairman. Advances in Chemistry Series, No. 34. American Chemical Society, Washington, D. C., 1962. vi + 260 pp. Figs. and tables. 15.5 × 23.5 cm. Paperbound. $8.

These papers, presented at the ACS meeting in September 1961, were selected to give both a review of the current state of several well-established polymerization process areas and a survey of new processes which appear to have interesting potential. The speed with which the symposium has been edited and published adds to its interest and importance. Since the material presented is often at the frontier of the polymer field, the book will mainly be of interest to the reader who already has some knowledge in the area—for example, the graduate student or teacher of a course in polymer science. These readers will find this book most worthwhile.

The processes are presented under the headings: Addition Polymerization, Polycondensation Reactions, and Commercial Polymerization Processes and Equipment Design. Some of the 21 topics included are: emulsion polymerization, Ziegler catalysis of dienes, radiation induced polymerization, ionic polymerization, effects of high pressure and low temperature, degradation of polymers, interfacial polymerization, prepolymer intermediates, heterocyclic polymerization, centrifugation of polymers and removal of solvent and unreacted monomer.

Because of the large number of authors and topics there is a wide range in breadth and depth of the chapters. The general level, however, is good. This book is a very commendable addition to the Advances in Chemistry series.

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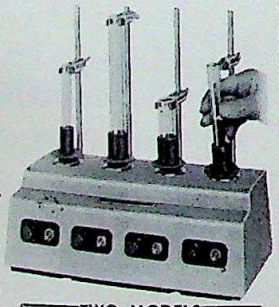
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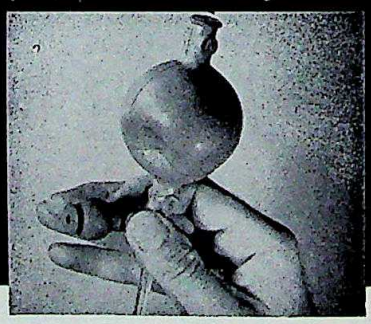
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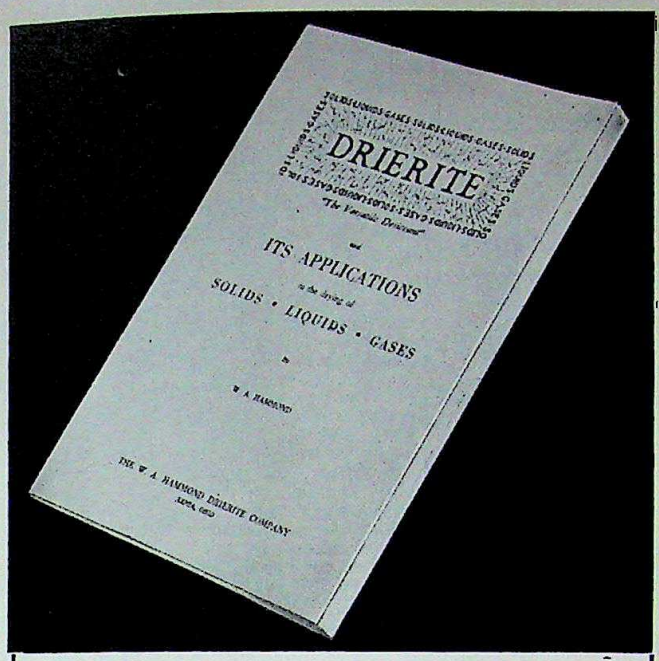
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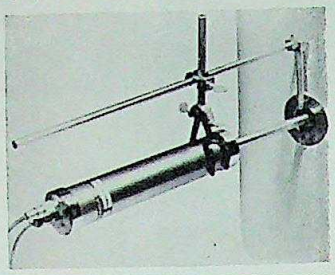
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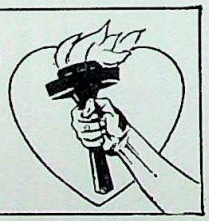
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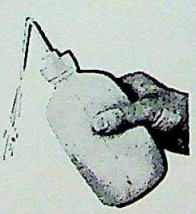
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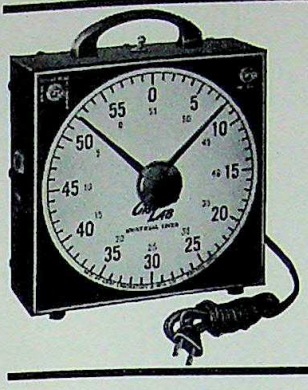
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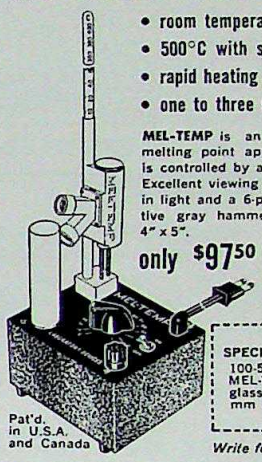
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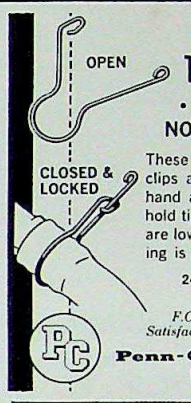
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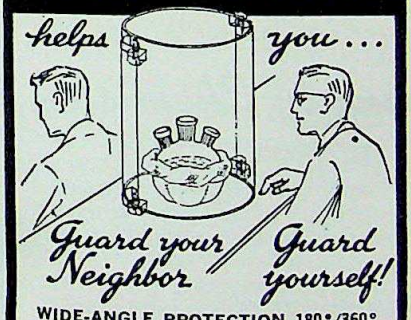
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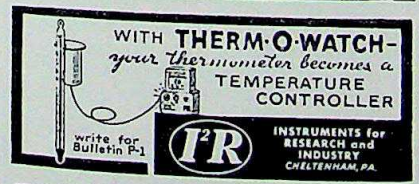
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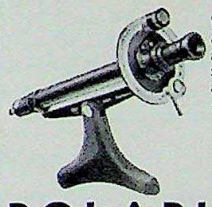
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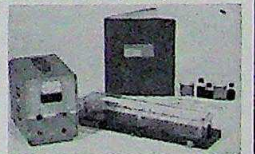
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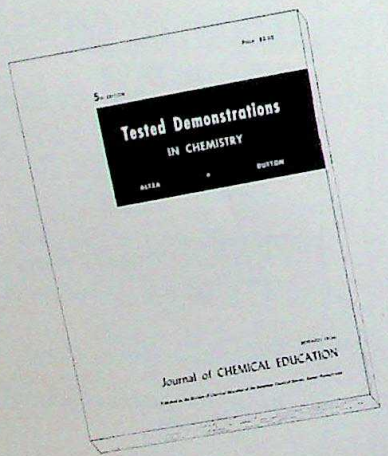
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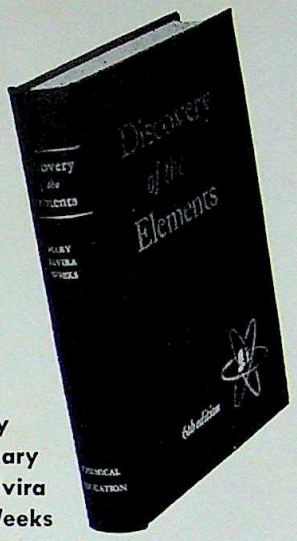
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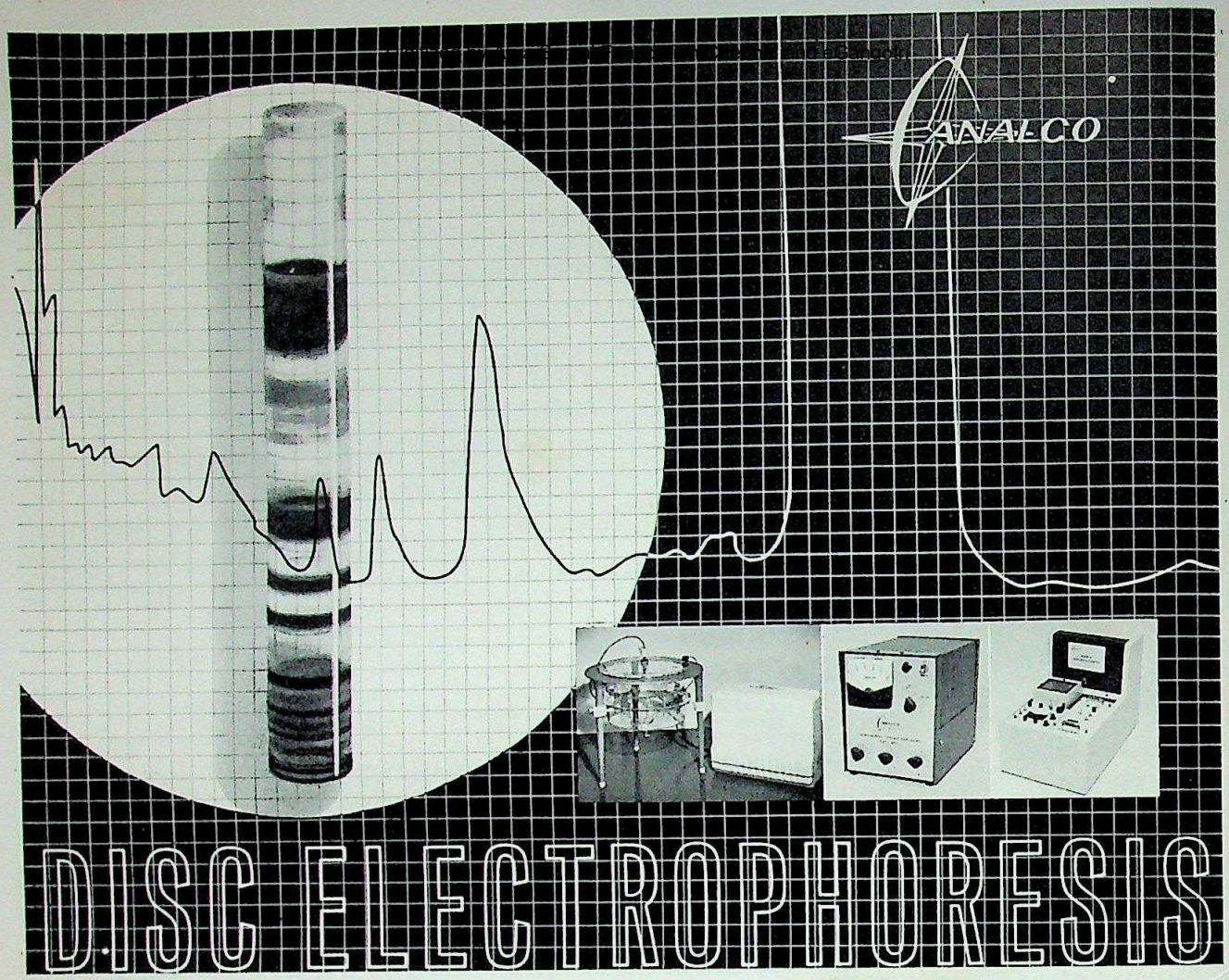
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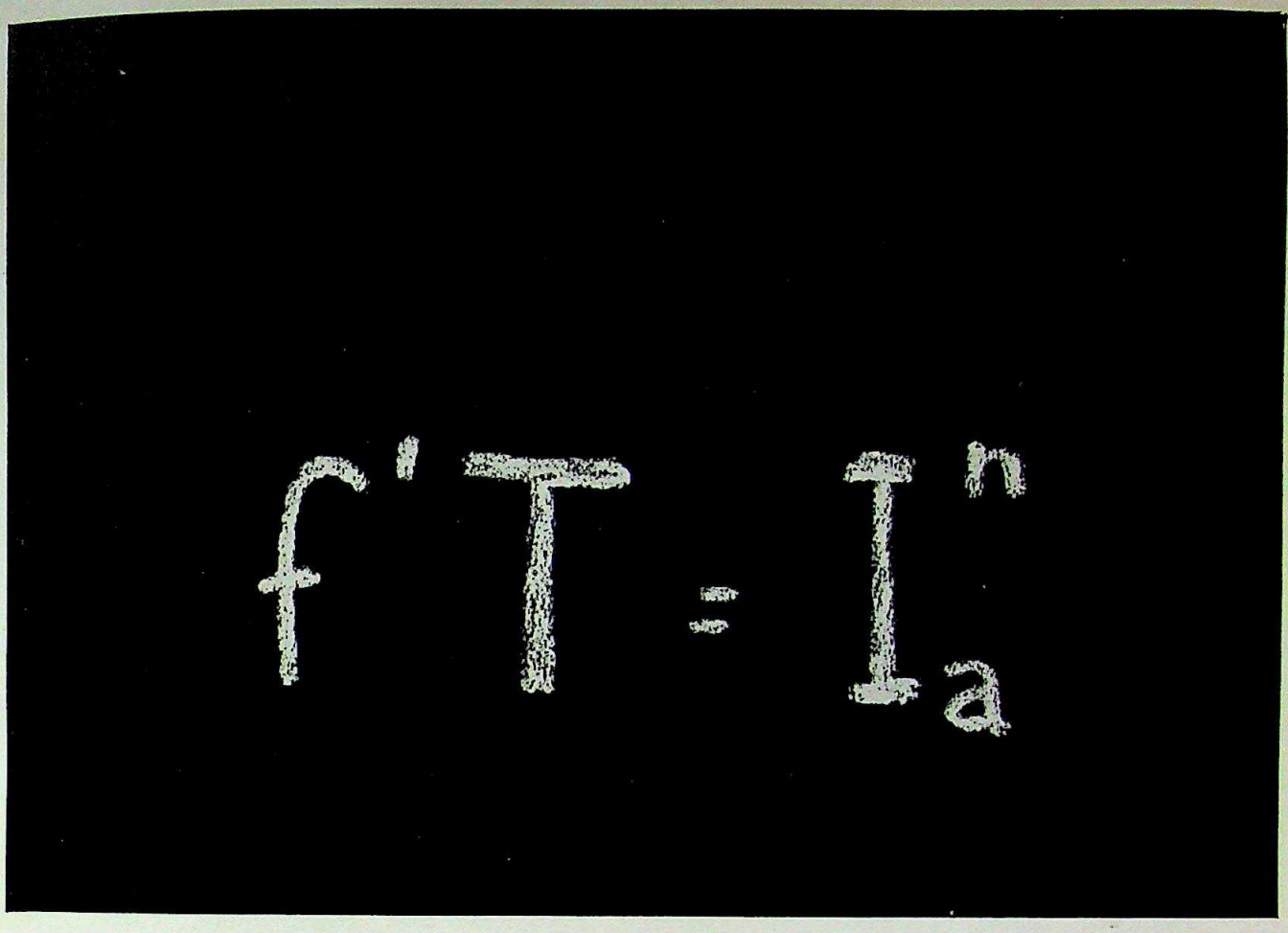
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SAMPLE OF THE CONTENTS

PART I

Chapter 1. Polynuclear Hydrocarbons. Phenanthrene. Anthracene. Anthraquinones. Reduction Products. Insect Dyes. Bacterial Pigments. Linear, Angular, and Condensed-Ring Hydrocarbons. Carcinogenic Hydrocarbons. Molecular overcrowding.

Chapter 2. Aromatic Heterocyclic Compounds. Furane, Pyrrole, and Thiophene. Pyrrole Pigments. Indole. Triazoles and Pentazoles. Phenylpentazole. Benzofuranes. Pyridine, Quinoline, Isoquinoline. Pteridines. Sydnones. Pyrones, etc. Anthocyanins, Flavones. Ommochromes. Boron Heterocycles.

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Edited by **S. Z. LEWIN,** New York University, New York 3, N. Y.

These articles, most of which are to be contributed by guest authors, are intended to serve the readers of this JOURNAL *by calling attention to new developments in the theory, design, or availability of chemical laboratory instrumentation, or by presenting useful insights and explanations of topics that are of practical importance to those who use, or teach the use of, modern instrumentation and instrumental techniques.*

VII. Chromatographic Glossary

The field of chromatography has shown more rapid and sustained growth during the past two decades than any other area of experimental chemistry. As a consequence, only a small part of the existing information and methodology has been organized in texts and monographs, and the user of chromatographic techniques must resort frequently to the original journal literature in order to find the data and procedures pertinent to his work. Multi-lingual glossaries of the special terminology of this field are an invaluable aid in this connection, and there is presented here two such glossaries, each in four languages. The first is taken from the recent book, "Dünnschichtchromatographie," E. Stahl, editor, Springer Verlag, Berlin, 1962, in which an excellent collection of the special terminology used in describing thin layer chromatographic techniques is given in German, English, and French. A corresponding set of the Spanish equivalents has been prepared for this Journal by Professors L. Condal and M. Montagut of the Instituto Quimico de Sarría, Barcelona, Spain.

The secondary glossary is composed of terms employed in the literature of gas chromatography. It has been prepared by H. M. McNair, F. and M. Scientific Europa, Amsterdam, and is available as a reprint from that company. In this case, too, the original glossary is in German, English, and French, and Profs. Condal and Montagut have provided the Spanish equivalents for the present publication.

For a detailed discussion of the general problem of the terminology of gas chromatography, the following articles will be found very informative: Ambrose, D. Keulemans, A. I. M., and Purnell, J. H., "Presentation of Gas-Liquid Chromatographic Retention Data," *Anal. Chem.*, **30**, 1582 (1958); Johnson, H. W., and Stross, F. H., "Terms and Units in Gas Chromatography," *ibid.*, **30**, 1586 (1958); Jones, W. L., and Kieselbach, "Units of Measurement in Gas Chromatography," *ibid.*, **30**, 1590 (1958).

Unfortunately, there are not available multi-lingual dictionaries that are adequate for the present needs of the experimental scientist. Two works that are of value for their coverage of certain portions of the field of modern specialized terminology, and of special languages, are: "Elsevier's Dictionary of Automation, Computers, Control, and Measuring," compiled on an English alphabetical base by W. E. Clason, Elsevier Publishing Co., 1961 (comprising six languages, viz., English/American, French, Spanish, Italian, Dutch, and German); "Dictionary of Chemistry and Chemical Technology," H. Stephen and T. Stephen, English Editors, Pergamon Press, 1962 (comprising four languages, viz., English German, Polish, and Russian).

A. Terminology of Thin Layer Chromatography

German	English	French	Spanish
abkratzen, abschaben	to scratch, to scrape off	détacher	desprender
absteigend	descending	descendant	descendiente
abwaschen, spülen	to wash, to rinse	laver, rincer	lavar
adsorbieren; Adsorption	to adsorb; adsorption	adsorber; adsorption	adsorber; adsorción
Aerosolpackung	aerosol package	cartouche d'aérosol	cartucho de aerosol
Aluminiumoxid	alumina	l'alumine	alùmina
Analysenmaterial, Gemisch	sample, mixture	l'échantillon, la prise d'essai, le mélange	muestra a analizar
anorganisch	inorganic	minéral	inorgánico
anwenden, Anwendung	to apply, application	utiliser, utilisation	utilizar, utilización
Arbeitsschablone	aligning tray	le gabarit	bandeja para alineación de placas (soporte para alineación de placas)
auflösen (eine Substanz in einem Lösungsmittel)	to dissolve	dissoudre	disolver
auflösen; Auflösung (Trennschärfe)	to resolve, to separate; resolution	séparer; séparation	separar; separación
aufsteigend	ascending	ascendant	ascendente
auftragen (eine Substanz)	to apply, to spot	appliquer	aplicar (a una muestra)
Band	band	la bande, la zone	la banda, la zona
basisch, alkalisch	alkaline	basique, alcalin	básico, alcalino
beschichten	to coat	recouvrir d'une couche	recubrir con una capa
beschriften, markieren	to mark	marquer	marcar, o señalar
Beschriftungsschablone	template for marking and sample applications	gabarit de marcage	plantilla para el marcador (plantilla para marcar y aplicar la muestra)
Bindemittel	binder	le liant	el adhesivo
BN-S-Trennkammer	BN-chamber, S-chamber	le cuve de séparation BN, S	la cubeta de separación BN, S
Dicke	thickness	l'épaisseur	el espesor

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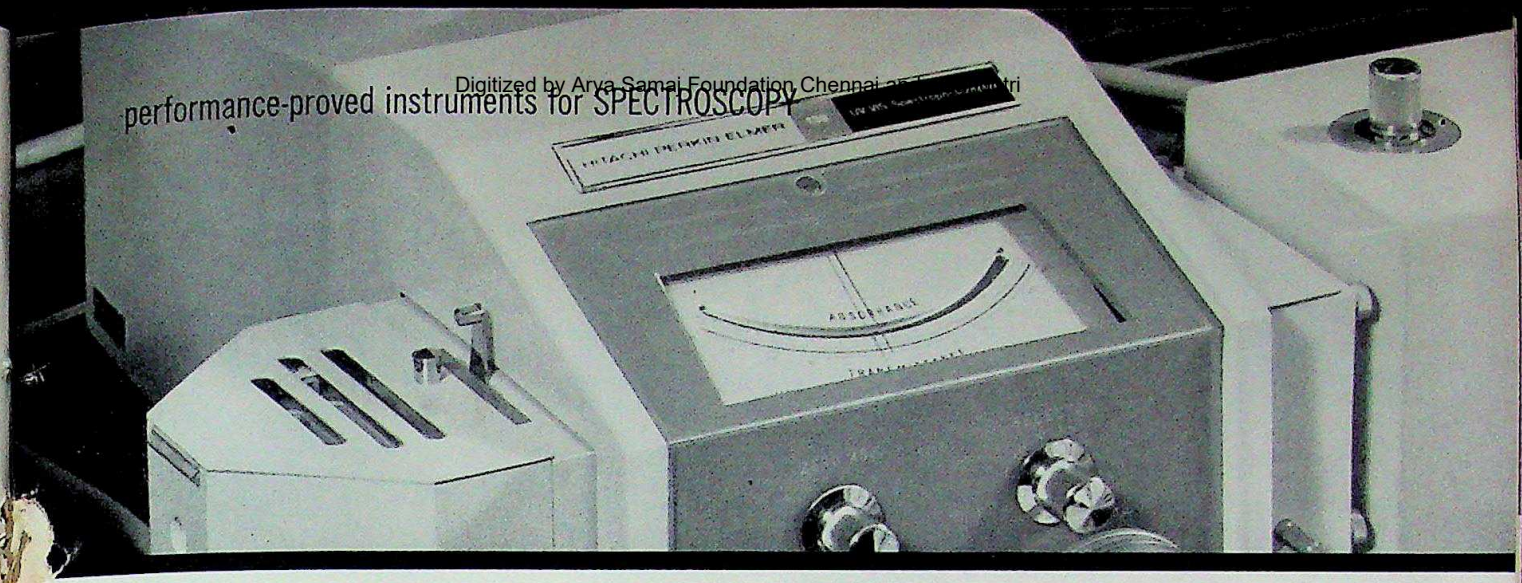
German	English	French	Spanish
Dünnschicht-Chromatographie, DC	thin-layer chromatography, TLC	la chromatographie en couches minces, CCM	la cromatografía de capa fina, CCF
dünnschichtchromatographisch getrennt	separated by TLC	séparé par chromatographie en couches minces	separado por cromatografía de capa fina o CCF
einheitlich, gleichmässig	uniform, even	homogène, régulier	homogéneo, regular
eintauchen; Eintauchen	to dip, dipping technique	immerger; l'immersion	sumergir, la inmersión
eluieren; Eluat	to elute; eluate	éluer; l'éluat	eluir, el eluido
Elutionsmittel	eluent	l'éluant, l'agent d'élution	el eluyente o agente de elución
entmischen	mixing	le démélange (démixtion)	demixtion
entwickeln; Entwickler	to develop, developer	révéler; le révélateur	revelar, el revelador
Exsiccator	desiccator	le dessiccateur	el desecador
farbig	colored	coloré	coloreado
farblos	colorless	incoloré	incoloro
Farbreagens	color reagent	le réactif colorant	reactivo cromogeno
Fixierbad	fixer	le bain de fixation	baño de fijado
Fleck	spot	la tache, le "spot"	la mancha
Fliessmittel	solvent (mixture)	le solvant	el disolvente
Fliessmittelfront	(solvent) front	le front du solvant	el frente del disolvente
flüchtig	volatile	volatil	volátil
Gaschromatrographie, GC	gas-liquid chromatography, GLC, gas chromatography	la chromatographie en phase gazeuse, CG	cromatografía en fase gaseosa, CG
Gefäss zum Entwickeln, Trennkammer, Tank	jar, tank, trough, vessel	la cuve	la cubeta, o recipiente
Gips (G)	calcinated calcium sulphate, gypsum, plaster of Paris	sulfate de calcium	sulfato cálcico
identifizieren; Identifizierung	to identify; identification	identifier; l'identification	identificar, la identificación
Ionenaustauscher	ion exchanger	l'échanger d'ions	intercambiador de iones
Keilstreifen-Technik	wedge-tip technique	la technique des bandes en cône	técnica de tiras en forma de cuña
Klebeband	tape, adhesive tape	la bande adhésive	cinta auto-adhesiva
Kieselgel	silica gel	le gel de silice	gel de silice
Kieselgur	diatomaceous earth, kieselguhr	le kieselguhr	kieselguhr
Kolonnen oder Säulen-chromatographie	column chromatography	la chromatographie sur colonnes	cromatografía de columna
Korngrösse	grain, size, particle size	la grosseur des grains ou des particules	tamaño del grano de las partículas
Laufgeschwindigkeit	speed of migration, travelling speed	la vitesse de migration de déplacement	velocidad de migración o desplazamiento
Laufstrecke	length of run	le parcours	el recorrido
mischen; Mischung	to mix; mixture	mélanger; le mélange	mezclar; la mezcla
Mörser und Pistill	mortar and pestle	le mortier et le pilon	el mortéro y la mano
Nachweis	detection	la détection, la révélation, la détermination, le dosage qualitatif	detección cualitativa o revelado
neutral	neutral	neutre	neutro
Papierchromatographie, PC	paper chromatography, PC	la chromatographie sur papier, CSP	cromatografía sobre papel, CSP
Papierstreifen zur Kammersättigung	the wick for chamber-saturation	la bande de papier servant à la saturation de la cuve	tiras de papel para saturar la cubeta
Pulver	powder	la poudre	el polvo
quantitative Auswertung	quantitative evaluation	l'évaluation quantitative	evaluación cuantitativa
quantitative Bestimmung	quantitative estimation, determination	le dosage quantitatif	determinación cuantitativa
Rand	edge	le bord	el borde
Röntgenfilm	X-ray film	le film pour rayons X	la película sensible a los rayos X
sättigen, gesättigt	to saturate, saturated	saturer, saturé	saturar, saturado
sauer	acidic	acide	acido
Schicht	layer	la couche	la capa
Schwanz, Streifen	tail, streak	la queue de comète, la trainée	la cola
Schwanzbildung	tailing, tail formation	la formation de trainée, d'une queue de comèt	formación de cola
sichtbar machen, kenntlich machen, nachweisen	to make visible, to visualize, to indicate, to locate	révéler	detectar o revelar
Sorptionsmittel	sorbent	l'adsorbant, l'agent d'adsorption	adsorbente
Spritze	syringe	la seringue	jeringuilla
Spur	trace	la trace	traza
sprühen, der Sprüer	to spray; atomizer, sprayer, vaporizer, spray gun	vaporiser; le vaporisateur	vaporizar (pulverizar); el vaporizador (pulverizador)
Sprühreagens	spray reagent, indicator	le réactif à vaporiser	reactivo a pulverizar
Standard (Vergleichs)	standard, reference material	l'étalon, le témoin	sustancia patrón
Start (-punkt)	starting point, point of application (of the sample)	le point de départ	punto de comienzo o de aplicación de la muestra
Streicher (Dünnschicht-), Streichgerät für DC	(TLC-)spreader, applicator	le dispositif d'étalement à étaler, le dispositif d'application	extendedor de la capa
Streifen	strip	la bande	la tira

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German	English	French	Spanish
Strich	streak	la ligne	la línea
Stufentechnik	gradual development (technique)	technique par étapes	desarrollo gradual
Subfraktionierung	subfractionation	le sous-fractionnement	subfraccionamiento
Tageslicht	daylight	la lumière du jour	luz de día
Testfarben	test dyes	les couleurs témoines	colores de prueba
Tieftemperaturchromatographie	low-temperature chromatography	la chromatographie à basse température	cromatografía a baja temperatura
Trägerplatte	the (glass) plate	le plaque support	placa soporte
Trennschärfe	resolution, sharpness of separation	la précision de séparation	resolucion o agudeza de separación
trennen; Trennung	to separate, to fractionate, to resolve; separation, fractionation	séparer; la séparation	separar, la separación
Trennung-Reaktion-Trennung (TRT) Technik	separation-reaction-separation (SRS-) technique	la technique séparation-réaction-séparation (SRS)	técnica-separación-reacción-separación (SRS)
Trockengestell	drying rack, storage rack	le séchoir	estantería para secar
trocknen	to dry	sécher	secar
unpolar, nicht polar	non-polar	non polaire	no polar
unterscheiden	to differentiate, to distinguish	différencier, distinguer	diferenciar o distinguir
UV-Licht	UV-light	la lumière U.V., l'U.V.	luz ultravioleta
Verbindung (chemische)	compound	le composé chimique	compuesto químico
verdünnen	to dilute	diluer	diluir
Vergleichssubstanz (Testsubstanz)	standard	l'étalon, le témoin	sustancia de prueba
Verhältnis (Mischungs-)	ratio	le rapport	la relación
verstellbar	adjustable	réglable	ajustable
Verteilung	partition	le partage	la partición o partición
Verteilung in umgekehrter Phase	reversed phase partition	le partage en phase inversée	partición en fase invertida
Vorschrift (Arbeits-)	direction, procedure	la mode opératoire	instrucciones o metódica
wässrig	aqueous	aqueux	acuoso
Wanderungsgeschwindigkeit	migration rate, speed of migration	la vitesse de migration, de déplacement	velocidad de migración o desplazamiento
Zone	zone	la zone, la bande	zona o banda
zweidimensional	two-dimensional	bi-dimensionel	bi-dimensional

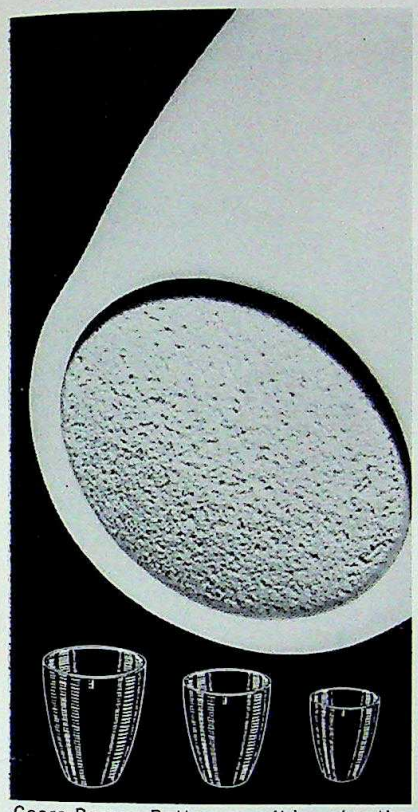
B. Terminology of Gas Chromatography

German	English	French	Spanish
Allgemeine Ausdrucke	**General Terms**	**Termes Généraux**	**Términos Generales**
Gas-Chromatographie	Gas chromatography (G.C.)	Chromatographie gazeuse	Cromatografía gaseosa
Gas-Flüssigkeits-Chromatographie	G. liquid C. (G.L.C.)	Chromatographie gaz/liquide	Comatografía gas-líquido
Gas-Feststoff-Chromatographie	G. solid C. (G.S.C.)	Chromatographie gaz/solide	Cromatografía gas-sólido
Vertrennung	Displacement	Déplacement	Desplazamiento
Elution	Elution	Élution	Elución
Frontal	Frontal	Frontal	Frontal
Isotherme Gas-Chromatographie	Isothermal G.C. (I.C.G.)	Chromatographie gazeuse isothermique	Cromatografía gaseosa isoterma
Mobile Phase	Mobile phase	Phase mobile	Fase móvil
Gelöste Substanz	Solute	Soluté	Substancia disuelta (soluto)
Lösungsmittel	Solvent	Solvent	Disolvente
Stationäre Phase	Stationary phase	Phase stationnaire	Fase estacionaria
Temperaturprogrammierte Gas-Chromatographie	Temperature programmed G.C. (T.P.G.C.)	Chromatographie gazeuse à température programmée	Cromatografía gaseosa a temperatura programada
Theorie	**Theory**	**Théorie**	**Teoría**
V.D. Gleichung	Van Deemter equation	Équation de V.D.	Ecuación de van Deemter
Theoretische Trennstufenhöhe	HETP (height equivalent to a theoretical plate)	Hauteur équivalente à un plateaũ théorique (HEPT)	Altura equivalente a un plato teórico
Streu Diffusion	A—eddy diffusion	Diffusion tourbillonnaire	Difusión parásita
Molekulare Diffusion	B—molecular diffusion	Diffusion moléculaire	Difusión molecular
Stoff Transport	C—mass transfer	Transport de masse	Transferencia de masa
Aktivitätskoeffizent	Activity coefficient	Coefficient d'activité	Coeficiente de actividad
Verteilungskoeffizent	Partition coefficient	Coefficient de partition	Coeficiente de partición
Siedepunkt	Boiling point	Point d'ébullition	Punto de ebulición
Schmelzpunkt	Melting point	Point de fusion	Punto de fusión
Konzentration	Concentration	Concentration	Concentración

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Porous BOTTOM Crucibles



Coors Porous Bottom crucibles give the chemist sturdy, dependable filtering crucibles for unlimited service under the most exacting conditions. An exclusive process developed by Coors provides a porous disc, formed into the crucible wall, that will not crack or drop out during use at room or elevated temperatures. The disc will not disintegrate when subjected to acids (except HF) or moderate alkali solutions. When these Coors crucibles are ignited even to extremely high temperatures, the porous disc will not crack, nor will the pore size be altered. Carefully controlled pore sizes are available in three ranges: (1) for bacterial separation and (2) fine filtering and (3) coarse precipitates. The crucibles are easily cleaned and readied for re-use. The same filtering disc may be ordered in the Coors Emich micro-filter stick for immersion filtration. Write for Bulletin No. 548. Coors Porous Bottom crucibles are immediately available through your nearest laboratory supply dealer.

INSIST THAT YOUR LABORATORY PORCELAIN WARE CARRY THIS MARK OF DEPENDABILITY

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COORS PORCELAIN COMPANY, GOLDEN, COLORADO

best buy in UV!

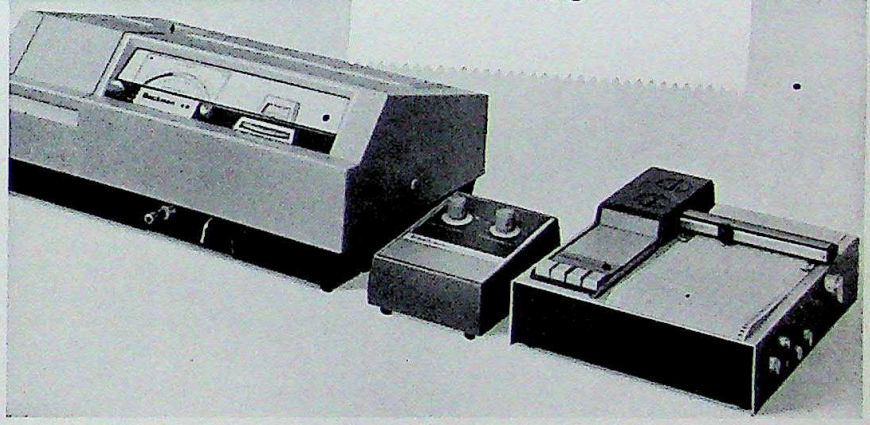
DB spectrophotometer

Linear and log recorder

Scale expansion accessory

TOTAL PRICE

$3270.00



You'd expect to pay twice as much for the performance and versatility you get with this UV-Visible Recording Spectrophotometer System.

Checkout these benefits –

Read concentrations from meter or recorder. Change from linear to log presentations at the flip of a switch to record transmittance or absorbance. And expand portions of both scales to full scale. Plus: full UV-visible range (205-770mμ), resolution better than 0.5 mμ, photometric repeatability exceeding 0.2%, variable scanning speeds, automatic 100% line stability. And much more.

Your Beckman Laboratory Apparatus Dealer has the complete story on this highly compatible trio. Also facts on how the Recorder (with its 22 accessories) and the Scale Expansion Accessory are used with other lab instruments. Contact him or write for Data File LUV-36-163.

Beckman®

INSTRUMENTS, INC.

SCIENTIFIC AND PROCESS INSTRUMENTS DIVISION

Fullerton, California

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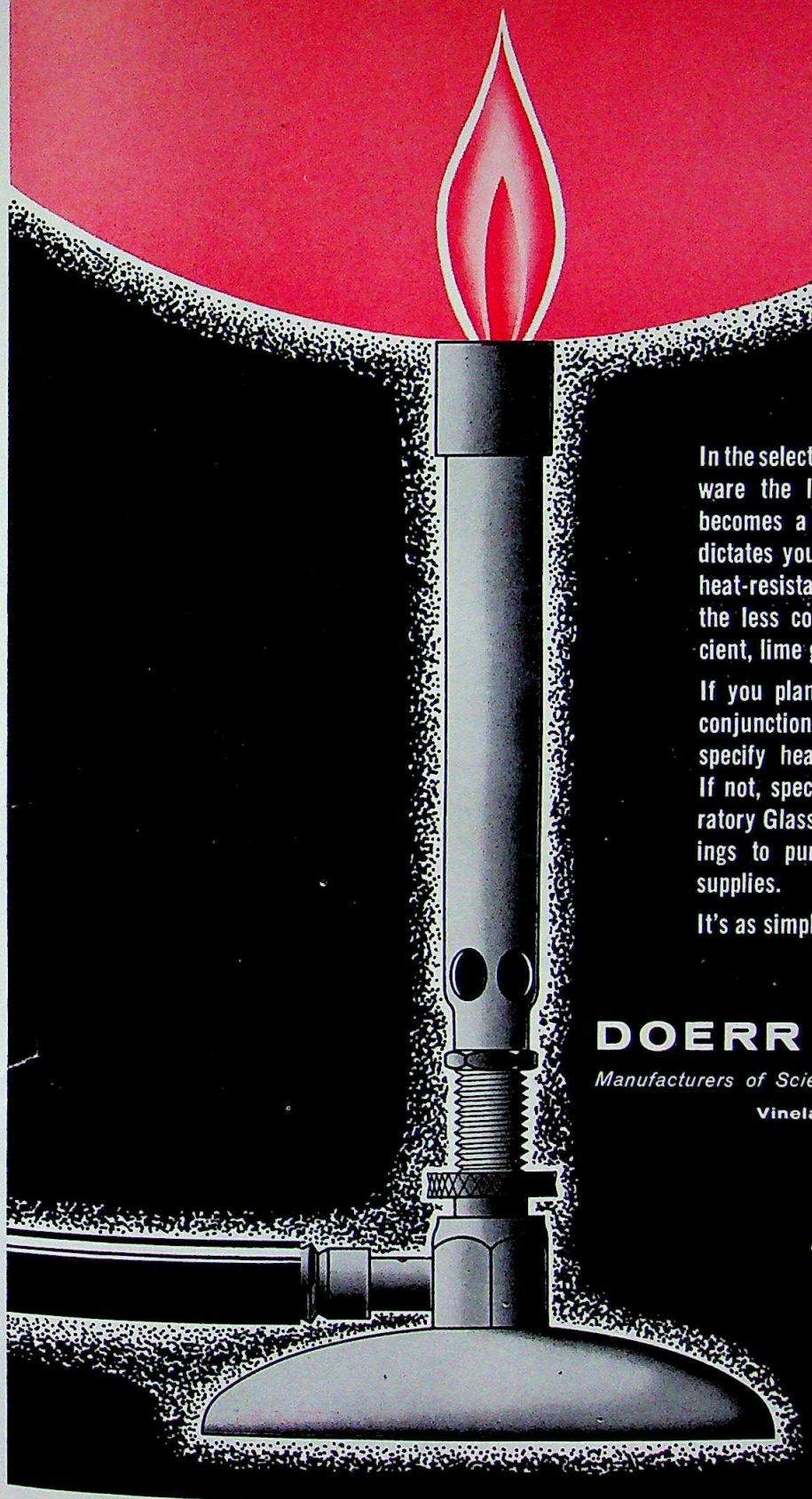
German	English	French	Spanish
Theorie	**Theory**	**Theorie**	**Teoria**
Diffusion	Diffusivity	Diffusibilité	Difusibilidad
Zwischen-Molekular-Kräfte	Intermolecular forces	Forces intermoléculaires	Fuerzas intermoleculares
Wärmekapazität	Heat capacity	Pouvoir calorifique	Capacidad caloríffica
Linear isotherm	Linear isotherm	Isotherme linéaire	Isoterma lineal
Molekulargewicht	Molecular weight	Poids moléculaire	Peso molecular
Beweglichkeit	Permeability	Perméabilité	Permeabilidad
Dampfdruck	Vapor pressure	Tension de vapeur	Presión de vapor
Viskosität	Viscosity	Viscosité	Viscosidad
Kolonnen-Wirkungsgrad	Column efficiency	Efficacité de colonne	Eficacia de la columna
(n) Theoretische Trennstufen	(n) theoretical plates	Plateaux theoriques	Platos teóricos
Lösungswirksamkeit	Solvent efficiency	Pouvoir solvant	Poder disolvente
Löslichkeitsunterschied (Selektivität)	Selective solvent	Solvant sélectif	Disolvente selectivo
Probeneingabe	**Sampling**	**Injection de l'échantillon**	**Inyección de la muestra**
Verunreinigung	Impurity	Impureté	Impureza
Probe	Sample	Échantillon	Muestra
Gemisch	Mixture	Mélange	Mezcla
Reine Komponente	Pure Component	Composant	Componente puro
Gase	Gases	Gaz	Gases
Flüssigkeiten	Liquids	Liquides	Líquidos
Feststoffe	Solids	Solides	Sólidos
Probengeber für Gase	Gas sampling valve	Valve d'introduction de l'échantillon	Válvula de introducción de muestras gaseosas
Spritze	Syringe	Seringue	Jeringa
Feststoff Probengeber	Solid sampler	Dispostif d'introduction d'échantillons solides	Dispositivo de introducción de muestras sólidas
Automatische Probeneingabe	Automatic sampling	Injection automatique	Inyección automática
Kontinuierliche Probeneingabe	Continuous sampling	Injection continue	Inyección continua
Flüssigkeitseingabeort	Injection port	Chambre d'injection	Cámara de inyección
Dichtung	Septum	Membrane	Membrana
Leckfrei	Leak-free	Étanche	Estanco
Schnelle Eingabe	Rapid injection	Injection rapide	Inyección rápida
Reproduzierbar	Reproducible	Réproductible	Reproducibilidad
Stromteiler	Split system	Système de division	Sistema de división de flujo
Vakuum	Vacuum	Vide	Vacío
Trägergas	**Carrier Gas**	**Gaz Porteur**	**Gas Portador**
Kompressibilität	Compressibility	Compressibilité	Compresibilidad
Diffusionskoeffizent	Diffusivity	Diffusibilité	Difusibilidad
Ionisationspotential	Ionization potential	Potentiel d'ionisation	Potencial de ionización
Wärmeleitfähigkeit	Thermal conductivity	Conductibité thermique	Conductividad térmica
Viskosität	Viscosity	Viscosité	Viscosidad
Durchflusskontrolle	**Flow-Control**	**Controle de Débit**	**Control del Gasto**
Durchflussmesser	Flow-meter	Débit-mètre	Medidor de gasto
Gasgeschwindigkeit	Gas velocity	Vitesse du gaz	Velocidad del gas
Eingangsdruck	Inlet pressure	Pression d'entrée	Presión de entrada
Ausgangsdruck	Outlet pressure	Pression de sortie	Presión de salida
Druckabfall	Pressure gradient	Facteur de pression	Factor de presión
Durchflussregler (Nadelventil)	Restrictor	Réducteur	Reductor de presión
Rotameter	Rotameter	Rotamètre	Rotámetro
Ventil	Valve	Vanne ou valve	Válvula
Trägermaterial	**Solid Support**	**Support Solide**	**Soporte Sólido**
Chromosorb	Chromosorb	Chromosorb	Chromosorb
Glas-Perlen (Kugel)	Glass bead	Perle de verre	Bolitas de vidrio
Säure, Base, mit Wasser gewaschen	Acid, (base, water) washed	Lavé à l'acide, avec une base, à l'eau	Lavado con ácido (con álcali, con agua)
Kraft für die Zerkleinerung	Crushing strength	Résistance au broyage	Resistencia a la molienda
Inert, stabil	Inert	Inerte	Inerte (estable)
Korngrösse in Mesh-Einheiten	Mesh-size	Granulometrie	Dimensión de lás maleas
Korngrösse	Particle-size	Dimension des particules	Dimensión de las partículas
Porös	Porous	Poreux	Poroso

(*Continued on page A174*)

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DICTATOR!



In the selection of laboratory glassware the lowly Bunsen Burner becomes a veritable dictator. It dictates your choice of expensive heat-resistant borosilicate ware or the less costly, but equally efficient, lime glass.

If you plan to use glassware in conjunction with a Bunsen Burner, specify heat-resistant glassware. If not, specify Diamond D Laboratory Glassware and use the savings to purchase additional lab supplies.

It's as simple as that!

DOERR GLASS CO.

Manufacturers of Scientific and Laboratory Glassware

Vineland, New Jersey

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German	English	French	Spanish
Flüssige Phasen	**Liquid Phases**	**Phases Liquides**	**Fases Líquidas**
Nichtflüchtige Substanzen	Non volatile	Non volatile	No volátiles
Polar	Polar	Polaire	Polares
Temperaturgrenze	Temperature limit	Limite de température	Límite de temperatura
Dampfdruck	Vapor pressure	Tension de vapeur	Presión de vapor
Adsorptionsstoffe	**Adsorbents**	**Adsorbants**	**Adsorbentes**
Aluminoxyd	Alumina	Alumine	Alúmina
Holzkohle	Charcoal	Charbon actif	Carbón activo
Molekularsieb	Molecular sieve	Tamis moléculaire	Tamices moleculares
Vergiftet	Contaminated	Contaminé	Contaminado
Deaktiviert	Deactivated	Déactivé	Desactivado
Modifiziert	Modified	Modifié	Modificado
Regeneriert	Regenerated	Régénéré	Regenerado
Kolonnen	**Columns**	**Colonnes**	**Columnas**
Analytisch	Analytical	analytique	Analítica
Kapillare	Capillary	Capillaire	Capilar
Gepackt, gefüllt	Packed	Remplie	Llenada
Präparativ	Preparative	Préparative	Preparativa
Halb-präparativ	Semi-preparative	Semi-preparative	Semi-preparativa
Ring	Coiled	En spirale	En espiral
Gestreckt, gerade	Straight	Droite	Recta
U-Rohr	U-tube	Tube en U	En forma de U
Durchmesser	Diameter	Diamètre	Diámetro
Länge	Length	Longueur	Longitud
Aluminium	Aluminum	Aluminum	Aluminio
Kupfer	Copper	Cuivre	Cobre
Glas	Glass	Verre	Vidrio
Edelstahl	Stainless steel	Acier inoxydable	Acero inoxidable
Adapter (Anpasstück)	Adaptor	Adaptateur	Adaptador
Anschlüsse	Connections	Connections	Conexiónes
Abdampfen der flüssigen Phase	Column "bleeding"	Entraînement de la phase stationnaire de la colonne	Arrastre (sangrado) de la fase liquida
2-Kolonnenanordnung	Dual column	Double colonne	Columna doble
Einzelkolonnenanordnung	Single column	Colonne simple	Columna única
Ringformige Kolonnen	Annular columns	Colonnes annulaires	Columnas anulares
Serienschaltung von Kolonnen	Columns in series	Colonnes en série	Columnas en serie
Parallelkolonnen	Parallel columns	Colonnes en parallèle	Columnas en paralelo
Detektor	**Detector**	**Detecteur**	**Detector**
Differential	Differential	Différentiel	Diferencial
Integral	Integral	Intégral	Integral
Linearität	Linearity	Linéarité	Linealidad
Rausch	Noise Level	Bruit de fond	Nivel de ruido
Empfindlichkeit	Sensitivity	Sensibilité	Sensibilidad
Signal	Signal/noise	Signal/Bruit	Señal-ruido
Zeitconstante	Time constant	Constante de temps	Constante de tiempo
Wärmeleitfähigkeitsdetektor	Thermal conductivity cell	Cellule à conductibilité thermique	Detector por conductividad térmica
Hitzdraht-Element	Hot wire filament	Élément de détecteur à fils	Elemento de hilos calientes
Platin, Wolfram	Platinum, Tungsten	Platine, Tungstène	Platino, tungsteno
Thermistor	Thermistor	Thermistance	Termistor
Ionisationsdetektor	Ionization detector	Détecteur à ionisation	Detector a ionización
Flammenionisation	FID-Flame ionization	Ionisation par flamme	Ionización por llama
Zusammenstoss	Collision	Collision	Colisión
Meta-Stabile	Metastable	Metastable	Metaestable
Primäranregung	Primary excitation	Excitation primaire	Excitación primaria
Auslöschen, abkühlen	Quenching	Extinction	Amortiguamiento (extinción)
Strahlung	Radiation	Rayonnement	Radiación
B-Strahlen	B-Rays	Rayons Beta	Rayos beta
Schütz, Schützung	Shielding	Blindage	Blindaje
Flammen-Ionisations Detektor	**Flame Ionization Detector (F.I.D.)**	**Detecteur a Ionisation de Flamme**	**Detector de Ionización por Llama**
Beschleunigungsspannung	Accelerating voltage	Tension d'accelération	Voltaje de aceleración
Lufteintritt	Air diffuser	Diffuseur d'air	Difusor de aire

(*Continued on page A178*)

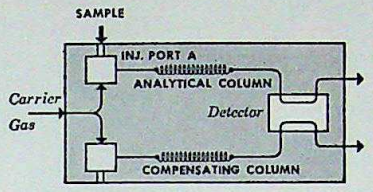
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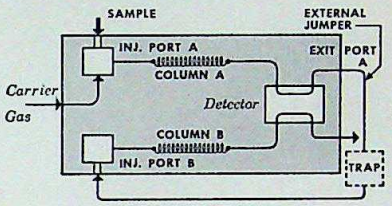
A major reason why so many chemists have praised the new F & M Model 720 Gas Chromatograph is the almost universal usefulness that results from the instrument's

a five-in-one chromatograph

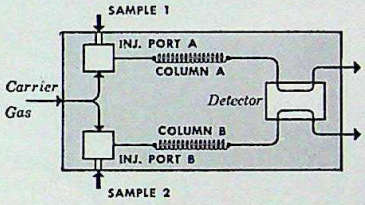
unique two-column design. The F & M designers equipped the Model 720 to provide five different column arrangements, each of which performs a valid function in the field of gas chromatography analysis.



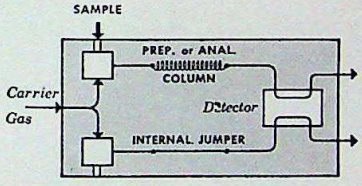
1 **Dual Compensating Columns**—In this flow configuration, the Model 720 eliminates the effects of substrate bleeding and extends by as much as 100°C the upper limit to which a column can be programmed without baseline drift.



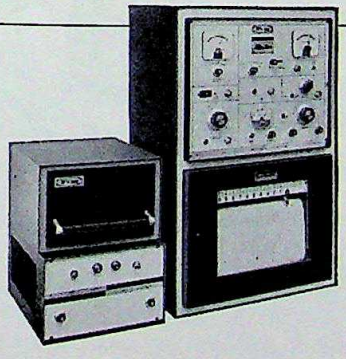
2 **Two Columns in Series**—In series operation, the 720 performs single-run analyses of difficult separations that require twice as much time on almost any other chromatograph. The analyst readily accomplishes series flow by connecting an external jumper between exit port A and injection port B.



3 **Two Independent Columns**—Used independently and with different packings, two columns are almost the equivalent of two instruments: they permit the analysis of duplicate or successive samples without downtime for column changes between analyses. No modification of the instrument is required.



4 **Preparative Column**—The Model 720 also provides the advantage of analytical separations on a preparative basis. For this purpose, standard F & M preparative columns are used. They permit the direct injection of large samples and the collection of very pure components directly from the exit port. As shown in the drawing, an internal jumper replaces the second column.



5 **Single Column**—Although designed specifically for dual column operation, the Model 720 serves equally well as a single column chromatograph. An internal jumper replaces the second column.

Changing from one of the five flow paths to any other is a minor operation of no more than a few minutes. Each of these methods is fully explained in the new F & M Bulletin 7200. For your copy, write or phone F & M Scientific Corporation, Starr Road and Route 41, Avondale, Penna., 215-COlony 8-2281.

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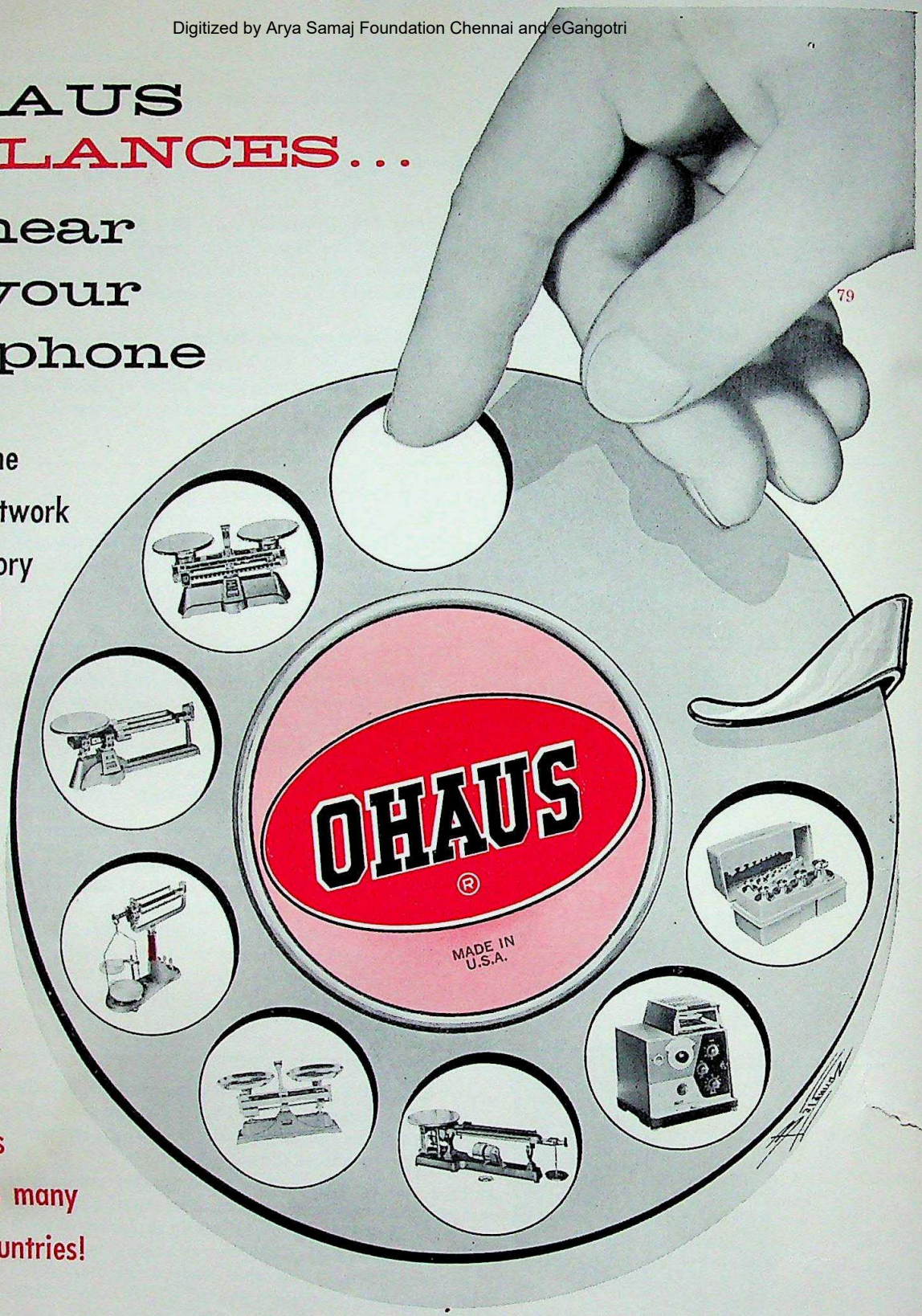
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COLEMAN

Coleman pH Instrumentation

Three pH meters and complete selection of electrodes meet full range of laboratory pH measurement requirements

Low-cost Metrion pH Meter is a line-operated instrument featuring a basic simplicity of design and operation which make it ideal for general-purpose laboratory use. With measurement accuracy to 0.05 pH, the Metrion provides a level of performance far out of proportion to its moderate cost.

Features:

- Stabilized against line voltage fluctuations over 95-125 volt range.
- Easy-to-read duplex scales cover 0-14 pH range.
- Calibration control provides compensation for temperature effect.
- Simplified operation—"push-to-read" pH control.

Cost—only $139.00.

Increased versatility, Metrion II pH Meter offers the same simplicity of design and operation as the basic Metrion. It also features two additional circuits for increasing versatility of the instrument:

...a true temperature-compensating circuit with a control knob conveniently located on instrument's front panel.

...an output jack for use with an automatic titrator such as the Coleman Titrion.

Addition of these two circuits makes the Metrion II valuable for an increased variety of specialized laboratory applications with only a small price increase.

Cost—$160.00.

Fully-versatile Companion pH Meter is a zero-restoring instrument ideal for a broad range of laboratory applications. It provides pH measurement over the 0-14 pH range with a routine accuracy of 0.05 pH and reproducibility within 0.02 pH. The instrument also may be used for millivolt measurements over a 1400 mv span.

Features:

- Zero-restoring circuit for drift-free operation.
- May be used with recorder, automatic titrator, and automatic temperature compensator accessory.
- Simplified control system for easy operation.
- Manual Temperature Compensator control permits accurate measurement over 0-100° C. range.

Cost—$300.00

Complete selection of electrodes—Coleman electrodes cover virtually every practical application of laboratory pH measurement. They are usable with any Coleman pH meter or other instrument of modern manufacture.

- Glass electrodes, shielded against stray electrical fields, permit precise measurement over widely-varying conditions of temperature, viscosity, alkalinity.
- Reference electrodes are available in standard calomel or non-mercurous types.
- Metallic electrodes for electometric titrations.
- Special-purpose electrodes for unusual applications.

Coleman electrodes are priced about one-third less than the closest competitive designs.

Write for full details



COLEMAN INSTRUMENTS, INC., MAYWOOD, ILLINOIS

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German	English	French	Spanish
Flammen-Ionizations Detektor	**Flame Ionization Detector (F.I.D.)**	**Detecteur a Ionisation de Flamme**	**Detector de Ionizacion por Llama**
Verstärker	Amplifier	Amplificateur	Amplificador
Automatische Zündung	Automatic ignitor	Allumeur automatique	Encendido automático
Koaxialkabel	Coaxial cable	Cable coaxial	Cable coaxial
Kollektorelektrode	Collector electrode	Électrode réceptrice	Electrodo colector
Elektrometer	Electrometer	Electromètre	Electrómetro
Duse	Flame tip (jet)	Extrémité de la flamme (Buse)	Tobera de la llama
Isolator	Insulator	Isolateur	Aislante
Oberfläche	Surface area	Aire	Sección
Elektronische Begriffe	**Electronics**	**Electroniques**	**Electronica**
Brückenschaltung	Balanced bridge	Pont équilibré	Puente equilibrado
Kondensator	Capacitor	Condensateur	Condensador
Heizpatrone	Cartridge heater	Cartouche de chauffage	Cartucho de calefacción
Strom	Current	Courant	Intensidad
Herz	Cycles	Cycles	Ciclos
Sicherung	Fuse	Fusible	Fusible
Erde	Ground	Terre	Tierra
Eisen-Konstantan Thermoelement	Iron-constantan thermocouple	Thermocouple fer constantan	Termopar hierro-constantán
Potentiometer	Potentiometer	Potentiomètre	Potenciómetro
Proportionalgeregelte Stromversorgung	Proportional power	Puissance proportionelle	Regulación proporcional
Gleichrichter	Rectifier	Redresseur	Rectificador
Widerstand	Resistor	Résistance	Resistencia
Kurzschluss	Short-circuit	Court circuit	Cortocircuito
Spannungskonstanthalter	Stabilized power supply	Alimentation stabilisé	Alimentación establizada
Transformator	Transformer	Transformateur	Transformador
Röhre	Tube (valve)	Tube électronique	Válvula electrónica
Variabel	Variac, Variable Transformer	Autotransformateur	Autotransformador
Spannung	Voltage	Voltage	Voltaje
Wheatstone'sche Brücke	Wheatstone Bridge	Pont de Wheatstone	Puente de Wheatstone
Chromatogramme	**Chromatograms**	**Chromatogrammes**	**Cromatogramas**
Korrekturfaktor	Correction factor	Facteur de correction	Factor de corrección
Todvolumen	Dead volume	Volume libre	Volumen muerto
Peakfläche	Peak area	Aire du Pic	Superficie de un pico
Peakhöhe, Breite, Basis	Peak base height, width	Hauteur, Largeur, Base du Pic	Base, alto y ancho de un pico
Relative Retention	Relative retention	Rétention rélative	Retención relativa
Retentionstemperatur	Retention temperature	Température de rétention	Temperatura de retención
Retentionszeit	Retention time	Temps de rétention	Tiempo de retención
Retentionsvolumen	Retention volume	Volume de rétention	Volumen de retención
Grundliniendrift	Baseline drift	Dérive	Deriva de la linea de cero
Peakform	Peak shape	Forme du pic	Forma del pico
Symmetrisch	Symmetrical	Symétrique	Simétrico
Tailing (Schweif)	Tailing	Trainée	Asimetrico (con cola)
Überlappung	Overlapping	Recouvrement	Yustaposición
Gut getrennt	Well-resolved	Bien séparé	Buena separación
Analyse	**Analysis**	**Analyse**	**Análisis**
Quantitativ	Quantitative	Quantitative	Cuantitativo
Qualitativ	Qualitative	Qualitative	Cualitativo
Normalisierung	Normalization	Normalisation	Normalización
Identifizierung	Identification	Identification	Identificación
Innerer Standard	Internal standard	Standard interne	Patrón interno
Zubehören	**Accessories**	**Accessoires**	**Accesorios**
Automatischer Empfindlichkeitsregler	Automatic attenuator	Attenuateur automatique	Atenuador automático
Rückspülsystem	Back-purge system	Système de purge	Sistema de retro-purga
Fraktionssammler	Collection system	Système de collection	Colector de fracciones
Verbrennungsrohr	Combustion tube	Four à combustion	Horno de combustión
Digitalintegrator	Digital integrator	Intégrateur digital	Integrador digital
Pyrolyseraum	Pyrolysis chamber	Chambre de pyrolyse	Cámara de pirólisis
Ersatzteile	**Spare Parts**	**Piéces Détachées**	**Piezas de Repuesto**
Gebläse	Blower	Ventilateur	Ventilador

(*Continued on page A184*)

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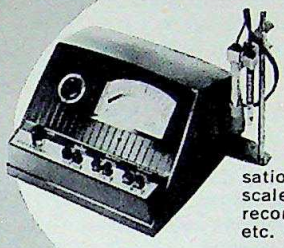
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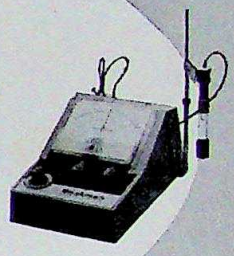
Spotlights pH Meters

With our comprehensive line of pH meters—including those made by Beckman, Coleman and Leeds & Northrup—we offer the proper instrument for your particular need.

Representative models are described below. We welcome your requests for more detailed information.



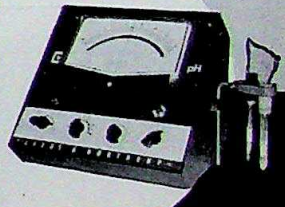
H-28915 BECKMAN Zeromatic pH meter, line operated. Simply push button and take pH or millivolt reading. Drift free, no warm-up time, line voltage compensation, continuous 0-14 pH scale. Outlets provided for recorder, polarizing current, etc. **$330.00**



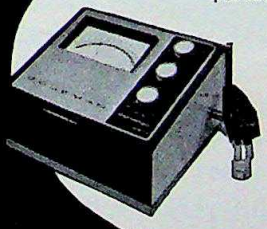
H-28925 BECKMAN Model 72 pH meter, line operated. This "Economy Model" has accuracy of ±0.1 pH and repeatability of ±0.05 pH. Suitable for Karl Fischer titrations. Used on liquids, pastes and semi-solids. Operates with only three controls **$184.00**



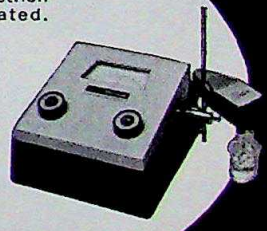
H-28905 BECKMAN Model 76 pH meter, line operated, for extremely precise pH and millivolt measurements. Features expanded scale. Any two pH units from 0 to 14 pH can be read with readability to 0.003 pH. Accuracy is ±0.02 pH. Of highest quality throughout. **$470.00**



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H-30035 COLEMAN Companion pH meter, line operated. This versatile meter with range of 0-14 pH and 0-1400 mv., reads directly from a single 6¼" mirror backed scale. Accurate within 0.05 pH, reproducible to 0.02 pH. A quality unit. . . . **$300.00**



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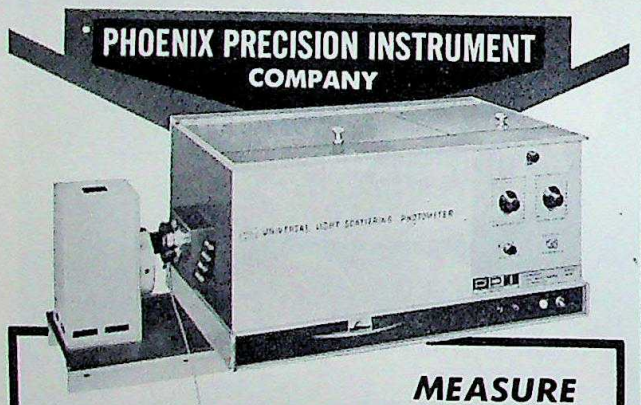
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Kolonnenheizung	Column heater	Chauffage de colonne	Calefacción de la columna
Thermostat	Column oven	Four de colonne	Termostato de la columna
Detektorblock	Detector block	Bloc de détecteur	Bloque detector
Detektorheizer	Detector heater	Chauffage du détecteur	Calefacción del detector
Getriebe	Gears	Engrenages	Engranajes
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Bedienungsanleitung	Instruction manual	Manuel d'utilisation	Instrucciones para el uso
Auswechselbare Teile	Interchangeable parts	Pièces interchangeables	Piezas intercambiables
Mikro-Schalter	Micro-switch	Micro interrupteur	Micro-interruptor
Motor	Motor	Moteur	Motor
Ein-Aus-Schalter	On-off-switch	Interrupteur	Interruptor
Tragbares Gerät	Portable instrument	Appareil transportable	Aparato portátil
Gedruckte Schaltung	Printed circuit	Circuit imprimé	Circuito impreso
Thermostat	Thermostat	Thermostat	Termostato
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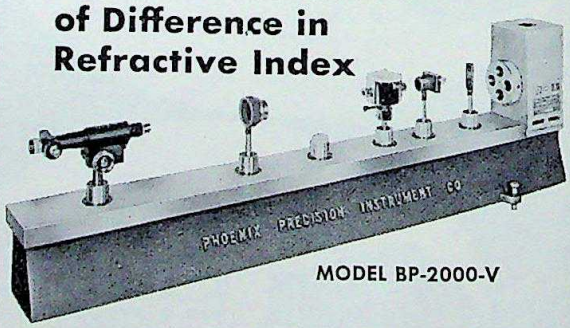
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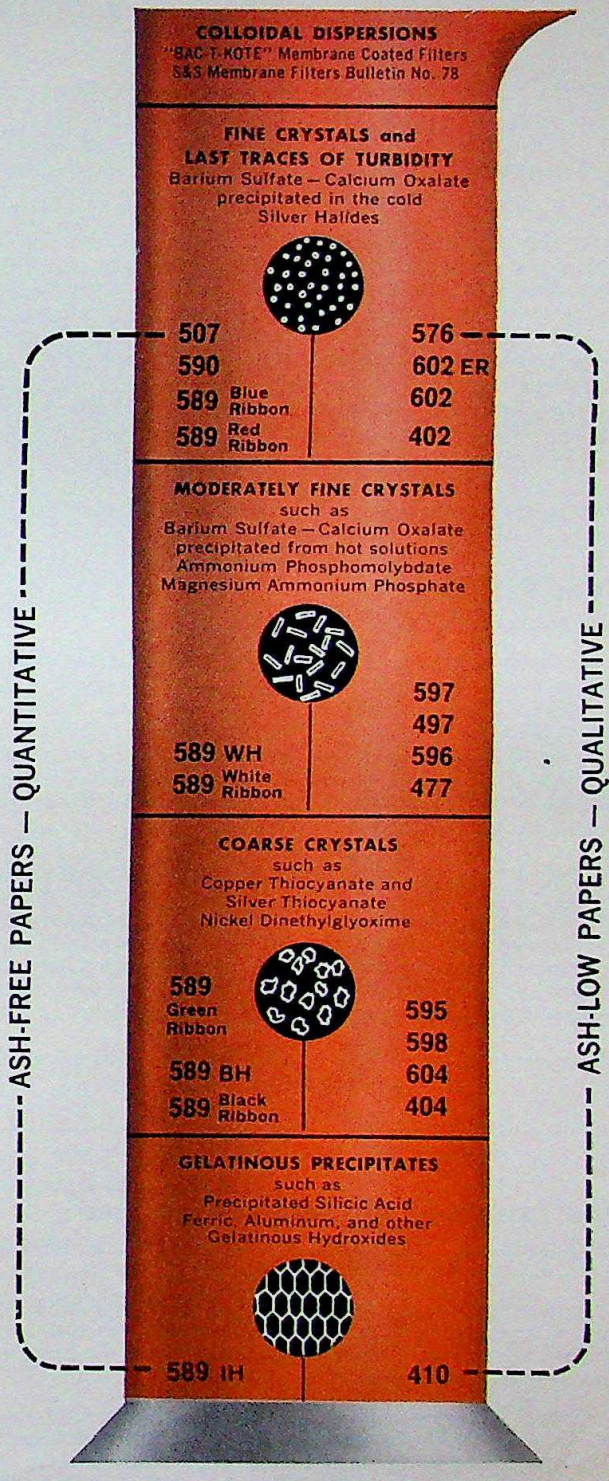
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CHEMICAL PROJECTS

Research Ideas for Young Chemists

Compiled by **JAY A. YOUNG,** King's College, Wilkes-Barre, Penna.
JOHN K. TAYLOR, National Bureau of Standards, Washington, D. C.

A Temperature Sensitive Stirring Rod

See: EDDY, R. D., AND SCHOLES, S. R., Jr., *J. Chem. Educ.*, **35**, 527–8 (1958).

Nitrogen(IV) oxide is prepared and transferred to a small tube, closed at one end and immersed in an ice bath. The top of the small tube is then sealed off. The procedure is essentially simple, though good technique is required and a beginner would probably not succeed in his first attempt. At moderately high temperatures the gas confined in the tube is largely NO_2; at low temperatures the dimer, N_2O_4, predominates. Since the momomer is colored and the dimer is colorless, the sealed tube can be used as a temperature sensitive stirring rod.

Question:

You have two choices if you wish to undertake an investigation in this field. Make a temperature sensitive stirring rod; or decide upon some other unique property of some other substance or mixture of substances and use that property to make a device which will have some utilitarian value.

NOTE: The nitrogen oxides are mildly poisonous; care should be exercised.

Zone Refining

See CHRISTIAN, J. D., *J. Chem. Educ.*, **33**, 32 (1956).

Zone refining is a highly efficient technique for the purification of a variety of materials. The process consists in the gradual transport of an ingot through a narrow molten zone. The slow solidification of the material at the cooling end of the molten zone results in a crystallization process in which impurities are rejected. Zone refining is used for the preparation of highly purified materials including silicon, tin, germanium, antimony, and various organic materials.

The reference cited above describes a simple procedure that is not only instructive in demonstrating the principle of zone refining, but should be useful in the purification of many low-melting materials. Essentially, the material is contained in a small-bore Pyrex tube that is passed slowly through a hot zone created by an electrical heating tape. Colored *p*-dichlorobenzene cakes and naphthalene are suggested as test materials.

The alert student will want to delve into practical applications as well as the theory of the technique. The article cites references that should be helpful in both respects.

Questions:

Construct apparatus for purification by zone refining and purify several materials by its use.

Look into methods for determination of the purity of the materials selected for refining and compare the efficiency of your zone-refiner with other methods of purification, e.g., solvent crystallization.

For a selected material, study the variables affecting the efficiency of zone refining, such as rate of transport through the molten zone, size of molten zone, diameter of "ingot," position of the tube.

The author points out that the removal of fluorescent impurities makes a dramatic demonstration. Could fluorescent impurities be added intentionally as tracers to indicate the efficiency of the process?

The Extraction of Metals from Ores

See KEUBEL, A., *J. Chem. Educ.*, 21, 148–9 (1944); GECKLER, R. P. AND MARCHI, L. E., *J. Chem. Educ.*, 21, 407–11 (1944); and STONE, C. H., *J. Chem. Educ.*, 21, 350, 436, and 439 (1944).

In these articles the authors discuss the extraction of four metals, uranium, indium, lead, and copper, from their ores. Sufficient details are given so that the extractions can be carried out by interested students.

NOTE: Because of the hazard involved, beginning students should not attempt the extraction of uranium from pitchblende. However, the general principles which apply to the winning of a metal from an ore in which it occurs in small amounts are discussed in the article by Keubel. This discussion will be helpful to students who elect to work in the area defined by the questions, below.

Questions:

Using one of the ores for which an extraction procedure is described in the cited articles, devise a different method for the extraction of indium, copper, or lead from the selected ore.

Select another ore containing indium, lead, or copper, but for which an extraction procedure is not described in the cited articles, and devise a suitable procedure for the extraction of metal from this ore.

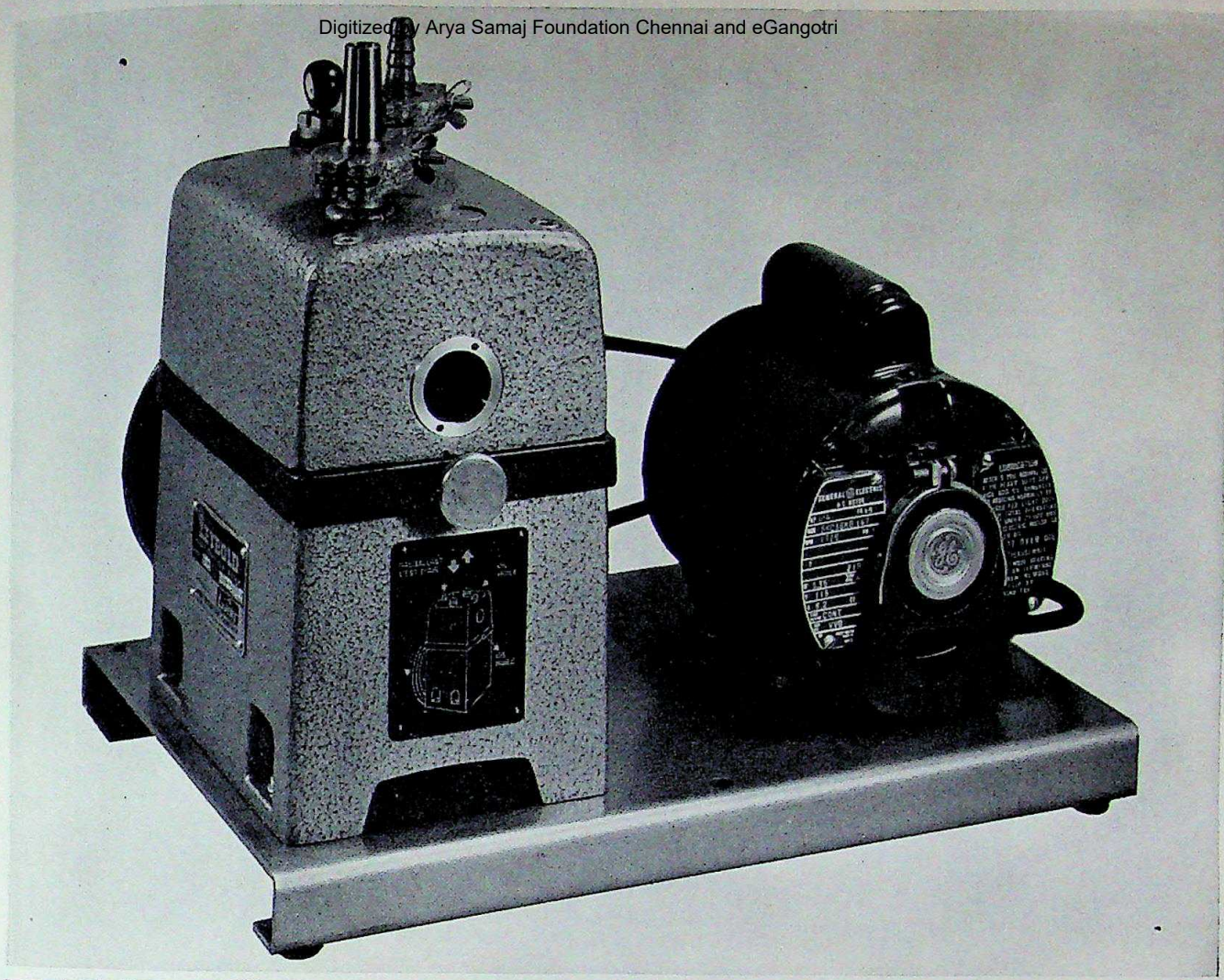
Select an ore of some other metal, and devise a procedure for the extraction of the metal, or metals, from this ore.

For any question, above, which you have elected to study, what is the efficiency of your process, in terms of the per cent of the metal, present in the ore, which you finally obtain in the metallic state?

For any question, above, which you have elected, can your procedure be improved either to yield the desired metal more economically, or in a state of higher purity?

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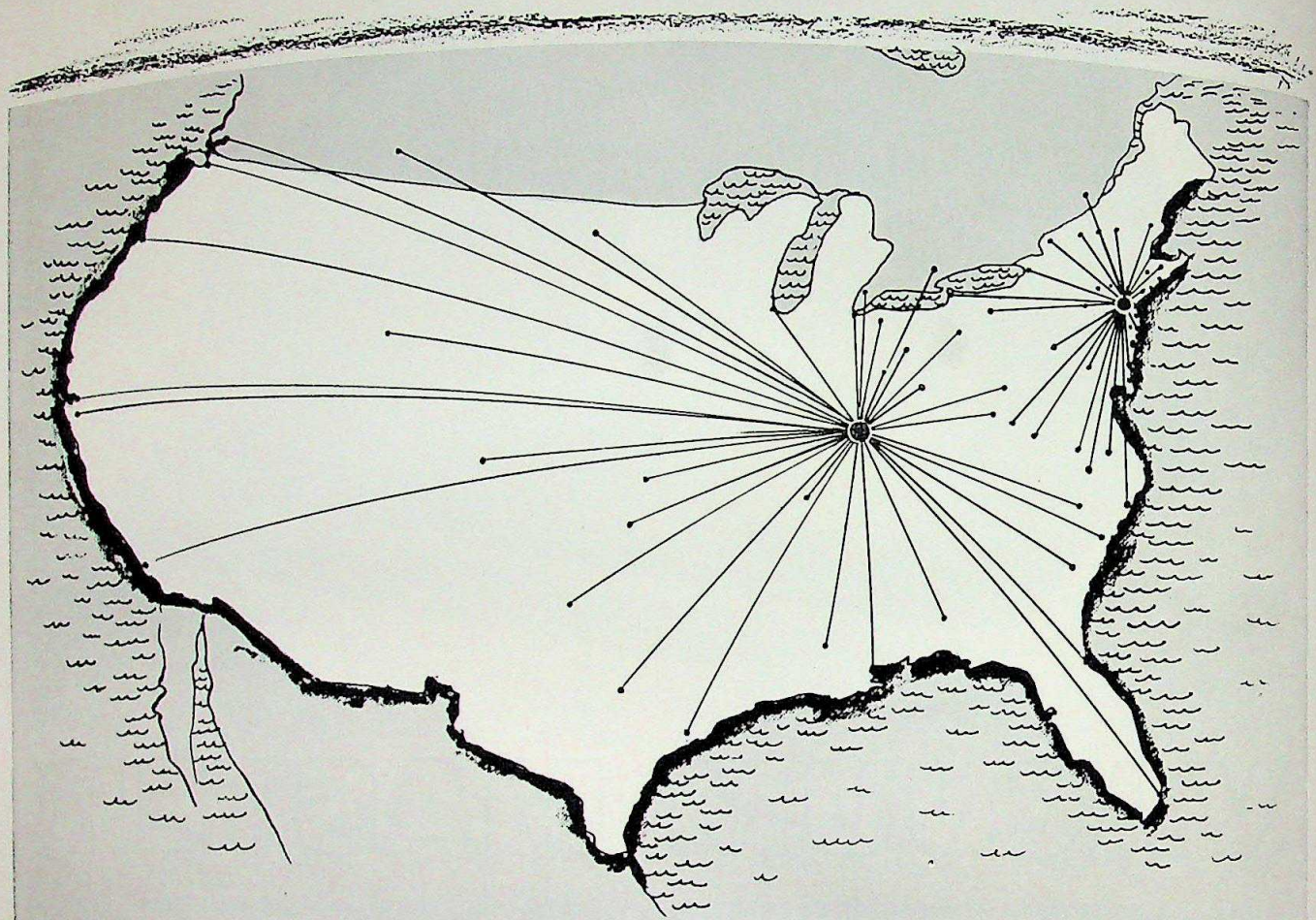
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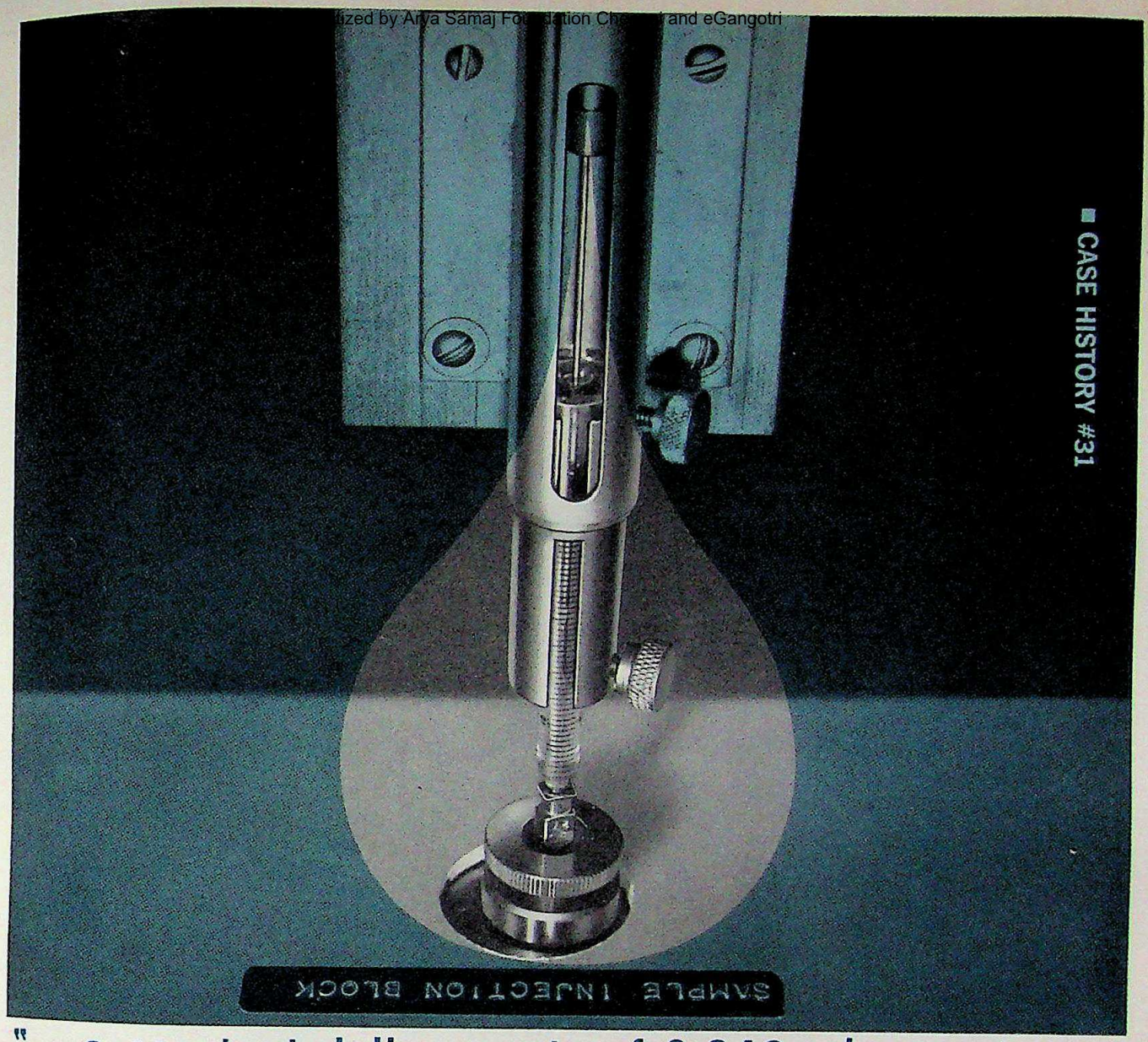
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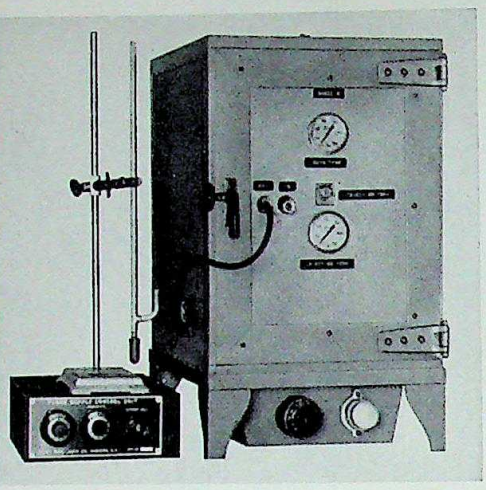
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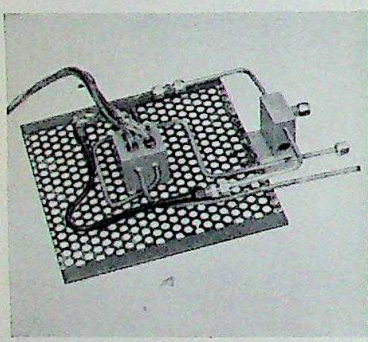
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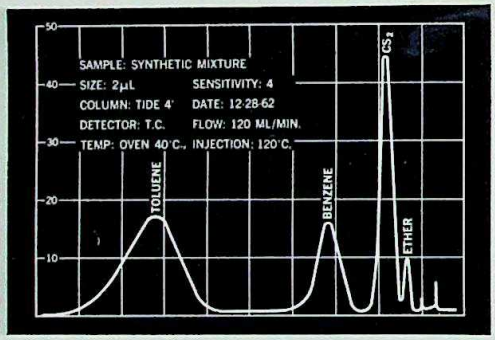
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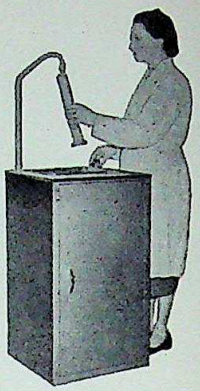
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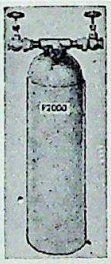


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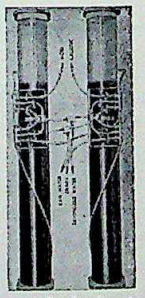
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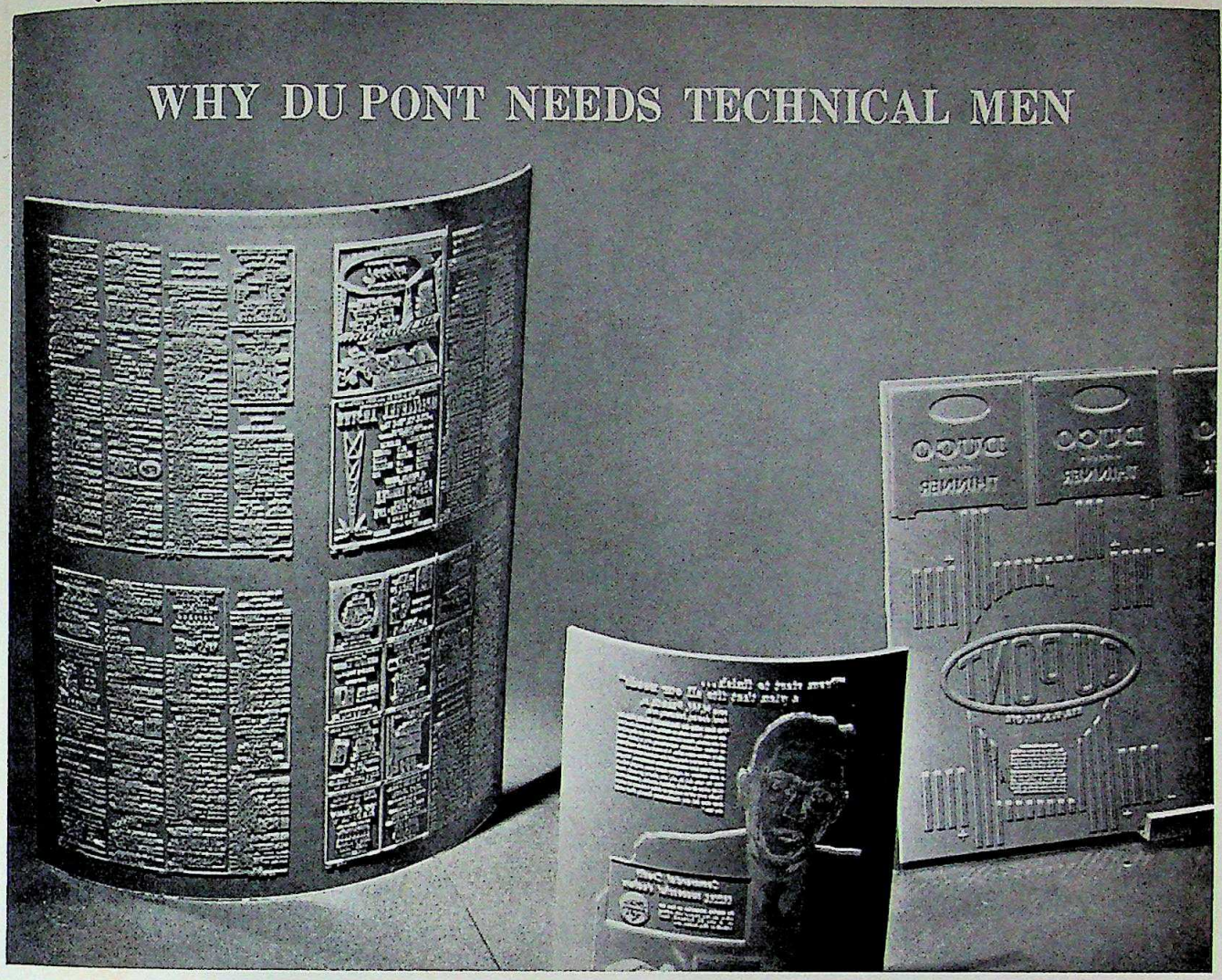
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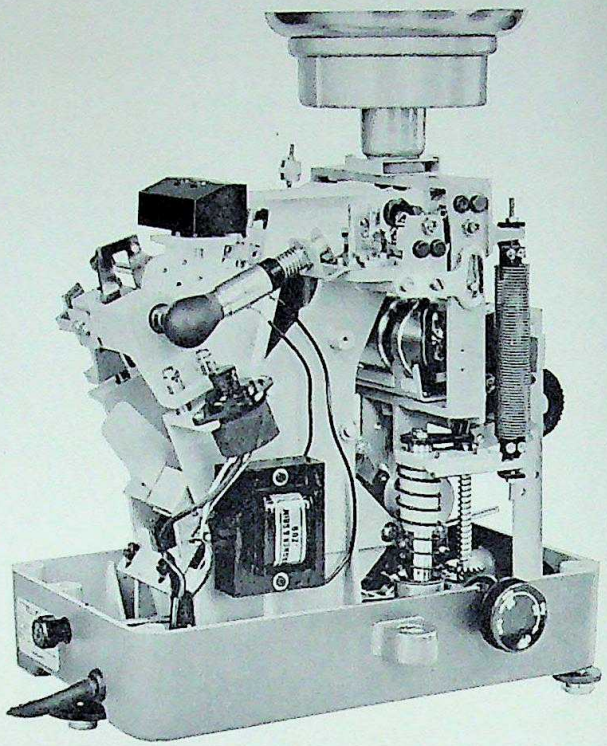
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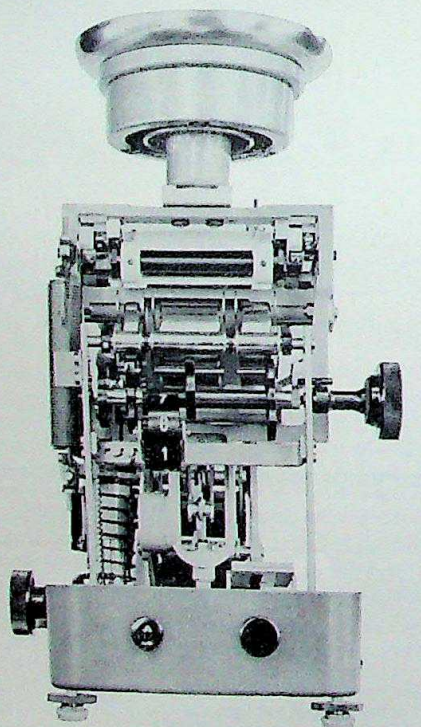
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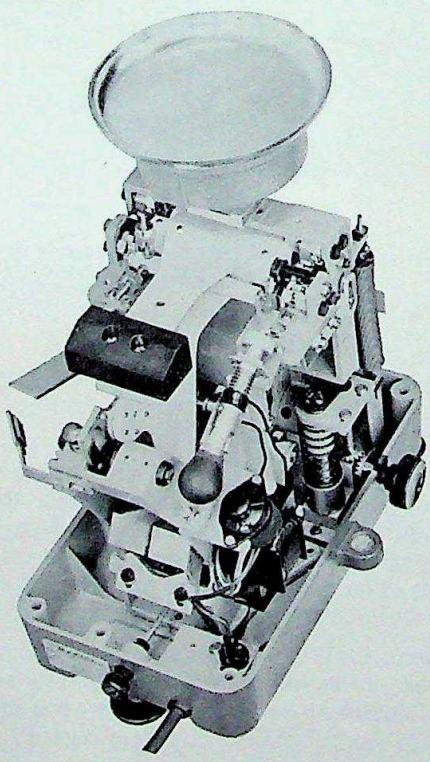
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it's the mechanism . . .



that measures . . .



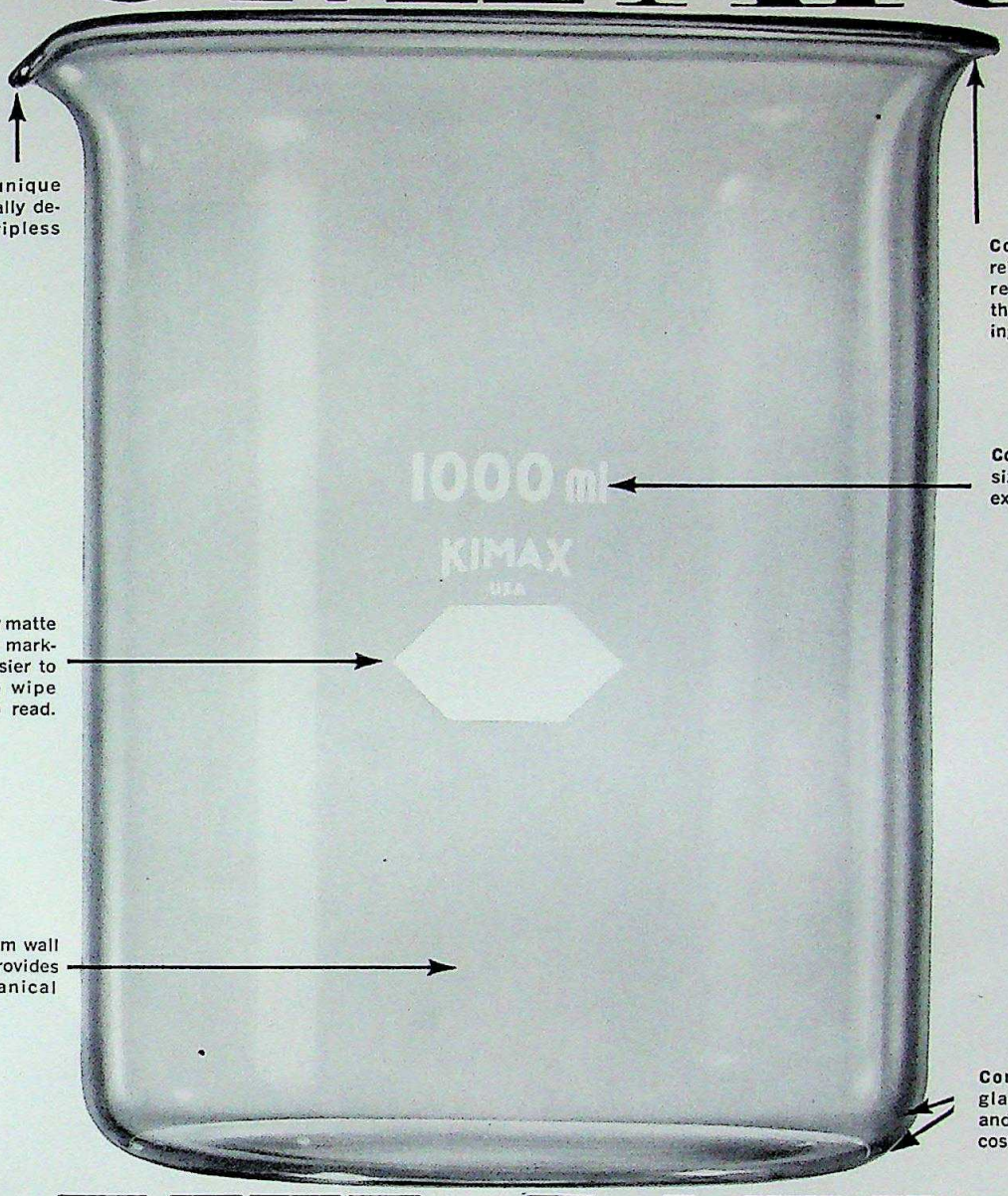
no matter how you look at it!

See the Mettler "K" Balance for yourself. Write for demonstration or particulars to:
Mettler® Instrument Corporation, 20 Nassau Street, Princeton, New Jersey

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COMPARE



Compare the unique pour-out especially designed for dripless action.

Compare the heavy reinforcing bead that resists chipping in the lab and in washing operations.

Compare the instant size selection through extra large markings.

Compare the new matte finish on larger marking diamond; easier to mark, easier to wipe clean, easier to read.

Compare uniform wall thickness that provides greater mechanical strength.

Compare the extra glass in shoulders and bottom that cuts costly breakage.

KIMAX®

Stand up a Kimax Beaker, Erlenmeyer, or Petri Dish side-by-side with other laboratory glassware. See for yourself why Kimax Brand glassware gives you more value, more life.

You get more of the better things first from Kimble.





Kimax Petri Dishes...
Bottoms and covers marked for faster sorting. Index arrows speed series dilution procedures.

Kimax Erlenmeyer Flasks...
Uniform glass thickness protects against thermal and mechanical shock. Heavy bead protects lip against chipping.

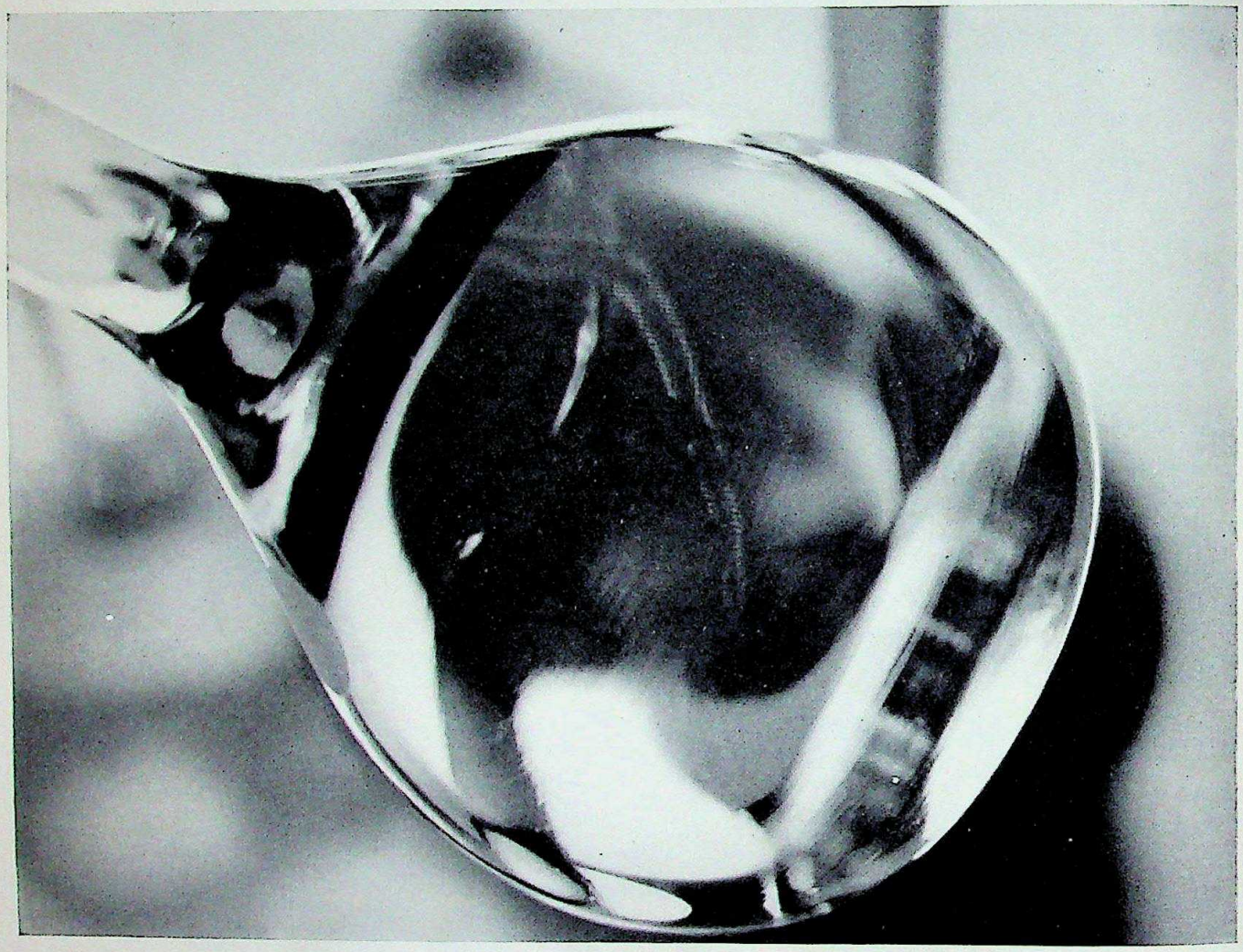
KIMBLE LABORATORY GLASSWARE
AN (I) PRODUCT

OWENS-ILLINOIS
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from abstract ideas...fundamental knowledge at Esso Research



Preferential solvation of the neutralization products is the major factor in determining the effects of solvents on the acidity and basicity of solutes according to studies by Dr. Orest Popovych, an Esso Research scientist. The equilibria between an indicator acid, bromophenol blue, and a series of heterocyclic amines in hydrocarbon and hydroxylic media have been described for the first time by a series of equations and constants. These can be evaluated by a combination of visible spectrophotometry (as represented by the above illustration) and electrolytic conductance. The ion-pair formation constant $K_B = (BH^+A^-)/(B)(HA)$ was adopted as the measure of basicity of an amine B relative to a reference acid HA.

It was found that while the relative strengths of the bases remained independent of the solvent, the absolute values of the K_B's were a sensitive function of the medium.

The acid-base reactions were most favored by polar and hydroxylic media. For example, adding isopropyl alcohol to toluene caused a rapid initial rise in reactivity which reached a plateau at about 5% of added alcohol. The addition of 0.5% water to a 50-50 isopropyl alcohol-toluene mixture produced a similar effect.

These indications together with other data make it clear that stabilization of ion pairs and ions by solvation seems to be the major factor in determining variation of acidity and basicity as a function of solvent.

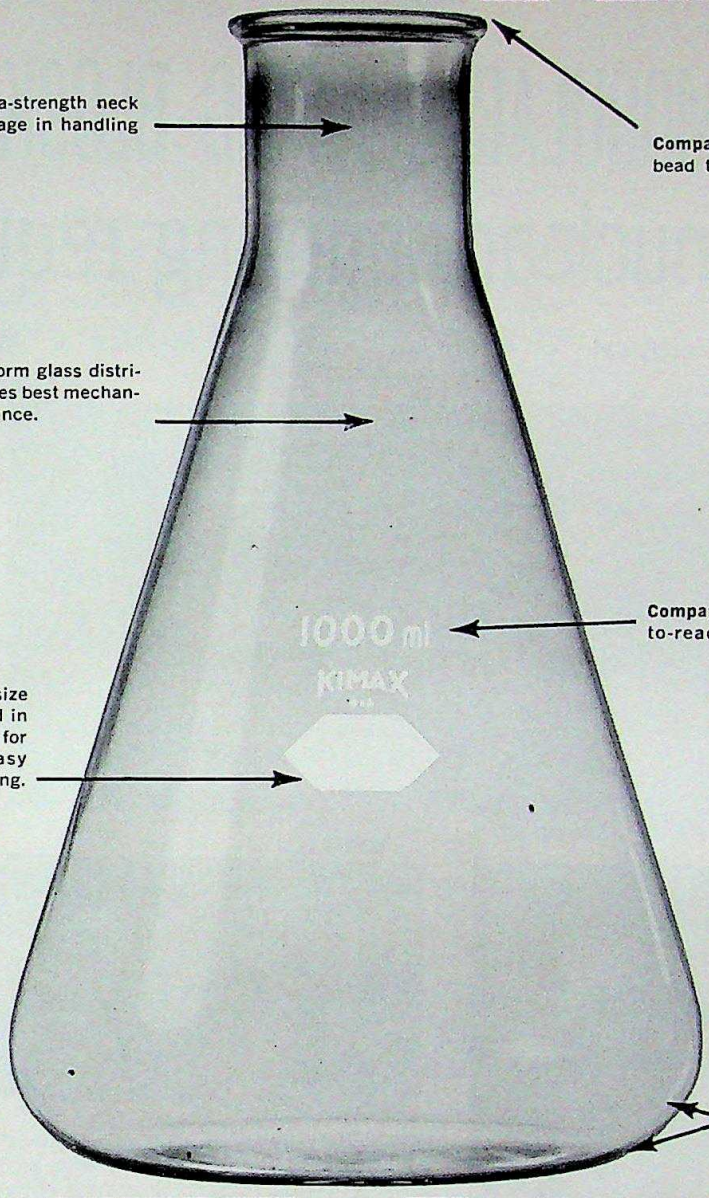
This new knowledge will permit more meaningful interpretation of acid-base phenomena and a more realistic approach to all research fields where nonaqueous media are involved.

...adapted from the scientist's notes at
Esso Research and Engineering Company
(P. O. Box 45B, Linden, New Jersey)
scientific affiliate of
Humble Oil & Refining Company

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COMPARE



Compare the extra-strength neck that resists breakage in handling and in washing.

Compare the extra reinforced bead that reduces chipping.

Compare the uniform glass distribution that provides best mechanical shock resistance.

Compare the extra-large, easy-to-read size identification.

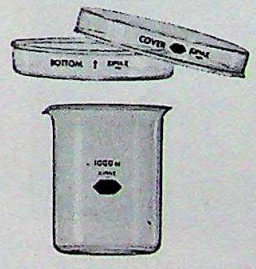
Compare the oversize marking diamond in new matte finish for easy writing, easy reading, easy erasing.

Compare the extra glass in shoulder and bottom that cuts costly breakage.

KIMAX®

Compare Kimax Beakers, Erlenmeyers, and Petri Dishes with other brands of scientific glassware. See for yourself why Kimax gives you extra value at competitive prices.

You get more of the better things first from Kimble.



Kimax Petri Dishes...
Markings save sorting time. Indexing arrow saves time and confusion in series dilutions.

Kimax Beakers...
Pour-outs specially designed to prevent dripping. Reinforced bead reduces edge chipping. New matte marking area is easy to mark, easy to read, easy to wipe clean.

KIMBLE LABORATORY GLASSWARE
AN (O) PRODUCT

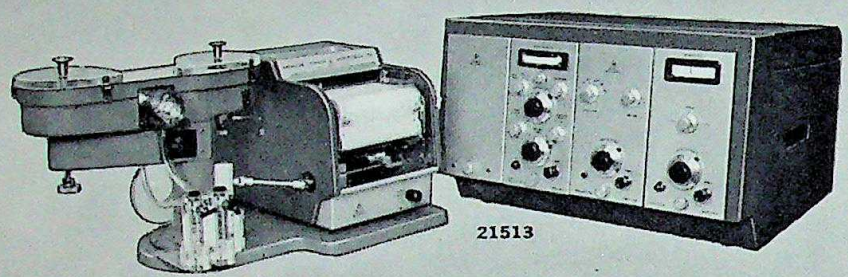
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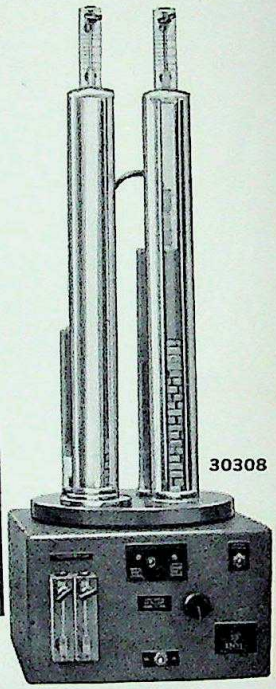
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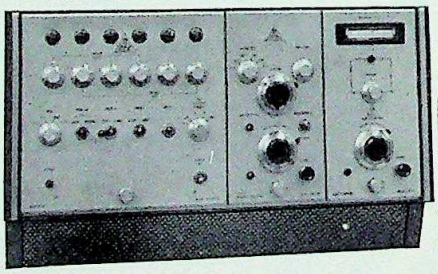
Biological • Chemical • Nuclear Physics • Medical



4 Pi Windowless Gas Flow Chromatogram Scanner with modular HV, ratemeter, and single channel analyzer. Replaceable scintillation detectors for gamma counting available. Request "Chromatogram Counting Systems."

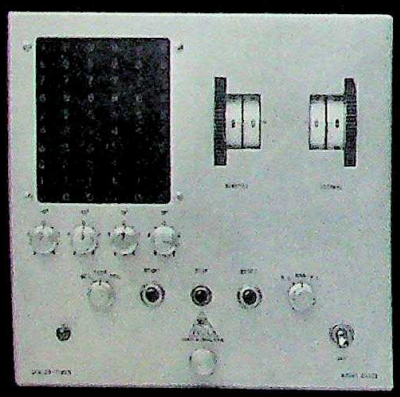


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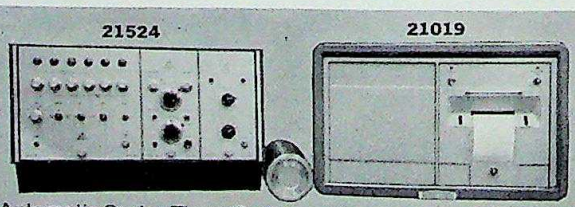
Automatic sample counting (up to 52 pans) with direct indication during count and automatic cycling. Detector available as gas flow windowless or scintillation crystal for gamma counting. Request Scaler-Timer System with 30308.

S-20323



New low cost Scaler-Timer module for scaling and single channel analyzer systems. Preset time increments in 0.01 minutes up to 90 minutes, accepts positive going 3 volt or negative going 250 mv pulse at 1 Mc, with one micro-second pulse pair resolution. Request S-20323.

21524 21019



Automatic Scaler-Timer System with automatic digital printout. Accepts wide range of inputs directly, using off-the-shelf modules. Request Scaler-Timer System 21524.

Complete specifications on the modular instruments which make up the RCL Building Block line available on request, ask for "Green Catalog."

RADIATION COUNTER LABORATORIES, INC.

5118 West Grove Street, Skokie, Illinois, U.S.A., TWX: 9675150, Cable Address: RACOLAB / Phone YOrktown 6-8700

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Chem Ed

Out of the EDITOR'S BASKET

Edited by William G. Kessel

When writing for additional information about new products or for new literature, your inquiry will receive prompt attention if you write on your firm or Institution letterhead and mention the Journal of Chemical Education and the date of the particular issue. Pamphlets, booklets and similar literature are gratis unless otherwise specified.

New Apparatus & Equipment

▶ For details on the Model 301 battery actuated chart drive or other Cannon products, write: L. J. Cannon Mfg. Co., Inc., 653 S. Melrose St., Placentia, California.

▶ Complete technical data available on the Lionel/Anton No. 455 ratemeter and scaler from Lionel Electronic Labs., Inc., Nuclear Division, 1226 Flushing Ave., Brooklyn 37, New York, Dept. NR.

▶ The completely transistorized 2672 survey meter is a portable alpha survey meter featuring solid state circuitry. It incorporates an air-proportional alpha detector that maintains complete insensitivity to beta and gamma radiation. Write Nuclear-Chicago Corp., 359 E. Howard Dr., Des Plaines, Illinois.

▶ A new all transistorized direct-reading gaussmeter for the measurement of magnetic fields is now in production by Alpha Scientific Laboratories, Inc., P. O. Box 333, Berkeley 1, California.

▶ The new multiple spindle magnetic stirrer recently developed by Eberbach Corp., P. O. Box 1024, Ann Arbor, Michigan, now provides laboratories with constant speed magnetic stirring as required in tissue culture applications, fermentation studies, and general purpose stirring.

▶ A new electronic unit, combining power supply and electrometer amplifier in a 5.5 × 15.5 × 19 in. chassis, is now available from Jarrell-Ash Co., 26 Farwell St., Newtonville 60, Massachusetts, for applications calling for accurate measurement of dc signals in the 10^{-11} to 10^{-5} amp range.

▶ Numec Instruments & Controls Corp., Apollo, Pennsylvania, announces the availability of a new analytical instrument, the Numinco Orr surface area-pore volume analyzer, Model MIC-101. This new all metal semiautomatic instrument determines not only surface areas of finely divided powders but also provides pore volume distribution data.

▶ A new instrument for rapid, semiautomatic analysis of blood gases has been developed by the Instrument Division of the Perkin-Elmer Corp., Norwalk, Connecticut. The unit also is suitable for the analysis of respiratory and other light gases.

▶ A new conductivity bridge, Model RC-18, featuring ±0.1% accuracy, has been made available by Industrial Instruments Inc., 89 Commerce Rd., Cedar Grove, New Jersey.

▶ For the safe, smooth, continuous transfer of fluids and gases, Greiner Scientific Corp., 22 N. Moore St., New York 13, N. Y., has introduced a newly perfected, air motor driven peristaltic pump with variable feed capability.

▶ A new booster tempunit for oil baths is now available from LaPine Scientific Co., 6001 S. Knox Ave., Chicago, Illinois. The new unit heats and stirs the oil or water medium, regulates its temperature and, if desired, circulates the liquid to an external apparatus such as a viscosimeter.

▶ A new, solid-state ratemeter, the Xenax, which combines the functions of an alpha counter, Geiger counter, ratemeter, neutron detector and fallout detector in one instrument has been developed by Atomic Laboratories, Inc., 3086 Claremont Ave., Berkeley 5, California.

▶ Mettler Instrument Corp., 20 Nassau St., Princeton, New Jersey, announces a new ultra-micro balance with readability

(*Continued on page A203*)



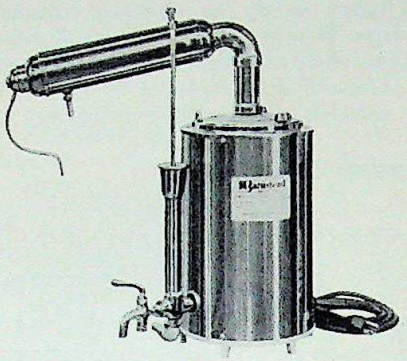
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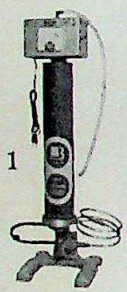
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BARNSTEAD
LABORATORY EQUIPMENT
FOR EXPANDING SCHOOL AND COLLEGE LABS

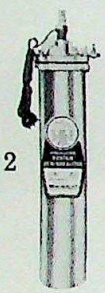
PORTABLE WATER STILL

Makes distilled water anytime, anywhere without the need of special tools, special connections and equipment. New Barnstead Portable Still can be plugged into any outlet handy to a sink . . . immediately produces ½ gallon per hour of the purest distilled water. No handling of bulky carboys. When not in use the Still stores in small space . . . 21″ wide x 19″ high x 10″ deep. Constructed of copper and brass, lined with pure block tin. Built to last 30 years or more. Produces distilled water for a few pennies per gallon.





1



2



3

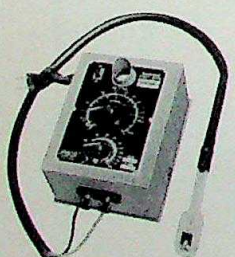
BANTAM DEMINERALIZERS

(1) Model BD-1, cartridge type demineralizer with direct reading meter, shows water purity at a glance. Flow rate: 5 to 10 gph, attaches to any faucet.

(2) Model BD-2, operated under pressure to 60 psig. Cartridges can be replaced quickly without tools. Pura-lite indicates when cartridge is exhausted. Flow rate up to 25 gph.

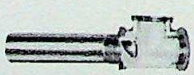
(3) Model BD-5, operated under pressure and has direct reading meter like BD-1. Flow rate up to 25 gph. Space required is 8″ x 8″ x 26″.

PURITY METER

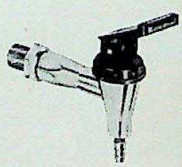


Barnstead Purity Meter provides a quick and easy check in determining the purity of either distilled or demineralized water being produced. Makes a purity check in just 30 seconds.

TIN-LINED PIPING AND FITTINGS







To maintain purity of distilled water to point of use, Barnstead offers a complete line of tin-lined piping, fittings and faucets. Piping may be permanently concealed between floors and walls with complete safety. Never any fear of breakage or leakage.

Barnstead®
STILL AND STERILIZER CO.

65 Lanesville Terrace, Boston 31, Mass.

WRITE FOR LITERATURE: Catalog "G" on Water Stills, Bulletin #175 on Purity Meters, Bulletin #173 on Portable Water Still, Bulletin #154 on Bantam Demineralizers.

MAKES IT PURE . . . . *KEEPS IT PURE*

ASK YOUR LAB SUPPLY DEALER

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the value of a dollar . . . movies without entertainment

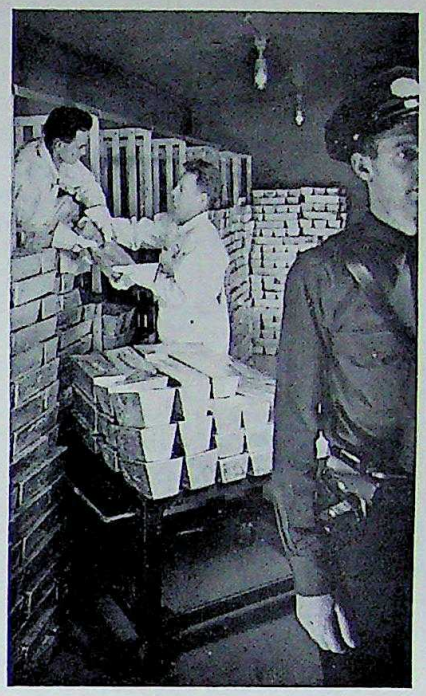
An interest in silver

To avoid crippling confusion in motivation, one stoutly reaffirms the belief of ages past that one is in business for the money. Today, however, other motivators exhibit their power, and though we still pursue the almighty dollar fiercely, once we have caught it we give little thought to the promise printed on it under President Washington's portrait. It promises silver.

Our house is founded on this truly unique gem of the periodic table. The marvelous behavior of the crystal lattice that it forms with bromine, when properly studded with impurities, makes photography possible; the importance of photography in both the serious and the gay is a major component of the force that attracted over 10^9 almighty dollars into the till last year. (Figuratively. Physically they are only a configuration of magnetized domains on a strip of iron oxide in some vault. Wonderful is the mind of man.)

Silver is drawn from the vault (a different vault) and made into pure $AgNO_3$. The vast bulk of this gets converted to silver halides and moves out on photographic goods. A very few parts per million find their way into bottles carrying the EASTMAN Organic Chemicals label.

Silver Nitrate itself, a fixture of the chemical laboratory since long before the invention of the test tube, still makes news. Only last spring it was revealed that silica impregnated with $AgNO_3$ displays highly selective adsorption with respect to the geometry and number of C=C's in related unsaturated lipids, as detailed for chromatographic practice in *Chemistry and Industry*, June 16 and



July 7, 1962. Last year also $AgNO_3$-Dichromate spray reagent was proposed for mercapturic acids and S-phenylcysteines (*J.C.S., 1962*, 608). $AgNO_3$ paper detects and fixes volatile As and Sb hydrides (*Chim. Anal.*, 43, 441). $AgNO_3$ is needed in the complexometric titration of K, Li, and Rb (*Mikrochim. Acta, 1961*, 644, 729, 732). Ol' $AgNO_3$ is still going very strong. It is one of the few soluble silver salts.

AgBr dissolves in water only to the extent of .00002g./100g. AgI and AgCl (but most emphatically not AgF) are similarly lower in solubility than merely poorly soluble silver compounds. An ion switch that produces one of these three will therefore pull through to completion. With appreciation for this simple fact, we offer:

Silver Nitrite (watch the spelling and call it EASTMAN 8671) to make certain nitroparaffins and nitroesters from halides, viz.

$$AgNO_2 + RX \rightarrow RNO_2 + AgX\downarrow$$
(*J.A.C.S., 76*, 3209)

Silver Arsenate (EASTMAN 8791) for bringing arsenic into organic chemistry by the reaction

$$Ag_3AsO_4 + 3RI \rightarrow (RO)_3As{=}O + 3AgI\downarrow$$

Silver Carbonate (EASTMAN 8777) for bringing carbonate into organic chemistry, e.g. $(R_4N)_2CO_3$

Acetic Acid Silver Salt (EASTMAN 8727, and aren't we silly in our nomenclature!) to make quaternary acetates by similar metathesis

Silver Cyanate (EASTMAN 1948) for introducing a cyanate radical and then arguing about the distinction between OCN^- and NCO^-

p-Toluenesulfonic Acid Silver Salt (EASTMAN 7912, "silver tosylate") which reacts with a primary aliphatic halide to precipitate the silver halide and yield the aliphatic tosylate, which, when added to a suspension of $NaHCO_3$ in *Methyl Sulfoxide* (EASTMAN P7108) at 150°C, loses its tosyl and leaves $CH_3(CH_2)_{n-1}CHO$ from what started out as $CH_3(CH_2)_nX$.

We also offer numerous reagents for *silver and an invitation to all chemists interested in silver to keep in touch with Eastman Organic Chemicals Department, Distillation Products Industries, Rochester 3, N. Y. (Division of Eastman Kodak Company). Some 4000 other* EASTMAN *Organic Chemicals which have nothing to do with silver can also be ordered from List No. 43.*

Brig. Gen. Webb's assignment

A physicist, a mathematician, and a few others talked one night at Woods Hole till dawn about the motion picture as a research tool and means of communication between scientists, quite apart from science teaching. They moved the National Academy of Sciences, the National Research Council, and the National Science Foundation. These imposing bodies have correlated their complex functions to seek out the scholar bending a movie camera to his will in some ignored nook of the campus. Their survey has turned up two or three hundred of him.

NSF has granted funds to the National Academy of Sciences to start the American Science Film Association. Brig. Gen. Willard Webb has left the Library of Congress to become administrative director of ASFA. The isolated researcher with a movie camera and the scientifically dead-serious businessman with priceless studies of whales copulating can look to ASFA. It will be able to tell one how others have solved problems he is still struggling with and to help him make contact with colleagues in various parts of the world who want to see *his* footage. He ought to make sure that his name and his interests are on file with American Science Film Association, 704 Seventeenth St. N.W., Washington 6, D. C.

Neither ASFA, NSF, NRC, nor NAS endorses any particular brand name, but we do. In doing so we can answer many pertinent questions about cameras, projectors, film, processing services, and auxiliary equipment for anybody who asks them of Eastman Kodak Company, Motion Picture Film Department, Rochester 4, N. Y.

This is another advertisement where Eastman Kodak Company probes at random for mutual interests and occasionally a little revenue from those whose work has something to do with science

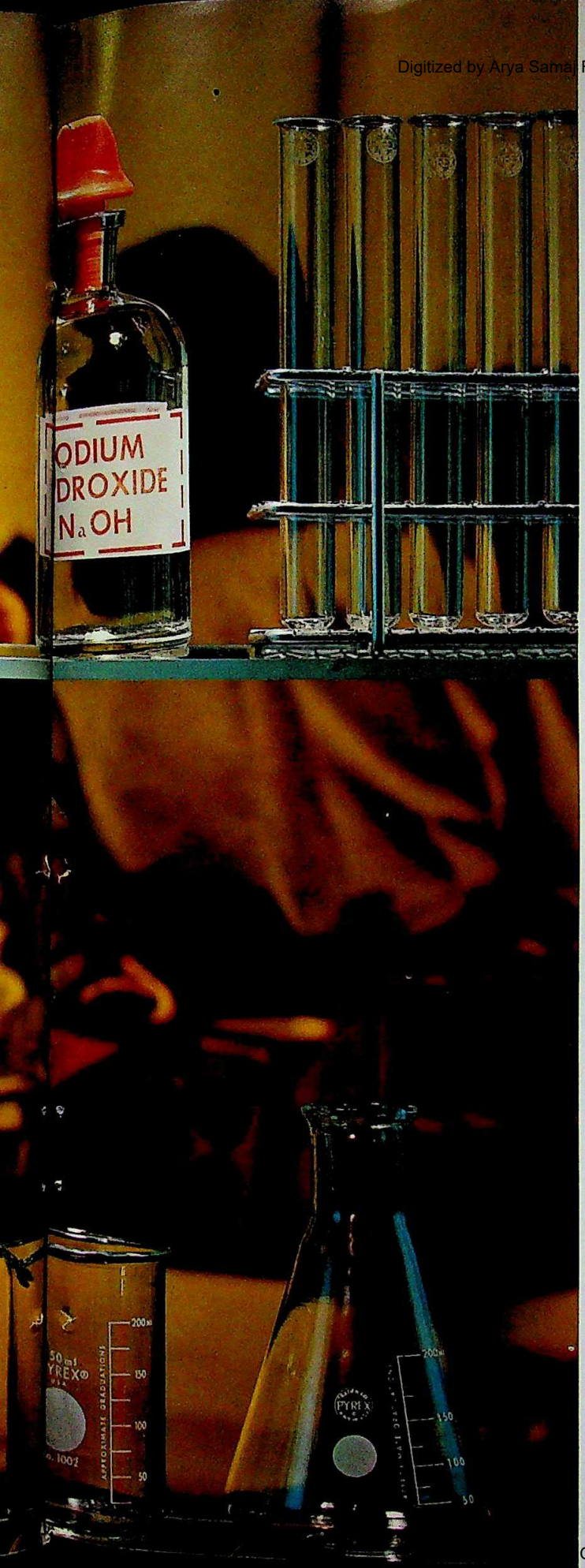
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Which of your students need PYREX® brand labware the most?

Maybe the precocious few. Don't they need the *thermal* strength of PYREX brand flasks, beakers, and test tubes? It gives you those extra seconds to find out what it is they've got over the burner.

Or maybe the awkward few. Don't they need the balanced *mechanical* strength of PYREX brand cylinders, beakers, and flasks? It protects them and their classmates from bumping, knocking, tipping accidents.

Or is it the majority? They need the professional look and feel and ease of use of *all* PYREX brand labware. It can help you teach them more in less time.

Don't *you* need PYREX brand labware, too—when you know it's designed and made to serve your students better, longer, and more safely? It costs you less, as well, because you get greater value out of its longer life.

Your laboratory supply dealer can help you get the most labware out of every dollar with our quantity-order discounts that can save you as much as 28¢ on every dollar's worth of PYREX brand labware you buy. The PYREX brand student items shown here are a good place to start. Laboratory Glassware Dept., Corning Glass Works, 7703 Crystal St., Corning, N.Y.

MEASURING BEAKER—mechanical and thermal safety in machine-formed walls and bottom. White enamel approximate graduations make it more versatile in your lab. No. 1002.

COLOR-CODED REAGENT BOTTLES—sharp, colorful labels and caps make student use even safer. Non-sticking polyethylene stoppers. No. 1552.

WEST CONDENSER—heavy-wall jacket and light-wall condenser tube give you strength for safety and faster condensing action to save precious lab minutes. No. 2700.

PINCHCOCK BURET—all the accuracy your students need at 40% **less** than the price of a ground stopcock model. No. 2118 buret and tip.

GRADUATED CYLINDER—clean, white, easy-to-read graduations. Tough, reinforced, hard-to-break rim and spout. Detachable hexagonal plastic base is unbreakable, cuts down tipping accidents. Cylinders and bases can be stored separately. Replacement cylinders are available. No. 3075.

BOILING FLASK—all the ruggedness, chemical stability, and heat resistance you need for student safety, at the price you need for economy. No. 4060.

GRADUATED ERLENMEYER—like the graduated beaker, this flask with approximate graduations is more useful to your students. The rim has been greatly reinforced to reduce chipping. No. 4982.

TEST TUBES—machine-made for uniform strength and safety. Rims make clamping easier and safer. No. 9800.

CORNING

THE MAKERS OF PYREX® BRAND WARE

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HIGH in VERSATILITY

LOW in PRICE

Entire control unit detaches for easy installation in another bath. This exclusive feature not offered in competitive units!

Typically outstanding Greiner quality... yet remarkably priced at about 50% less than competitive models of similar sensitivity!

NEW from GREINER

ALL-PURPOSE ECONOMY BATH



Newly designed constant temperature bath for general laboratory use features double-wall type construction. Water chamber is stainless steel, with glass wool insulation between stainless steel inner jacket and outer wall. Working dimensions: 22″ x 11½″ x 9½″ deep.

Three-heat selector switch offers settings of 400, 800 and 1,600 watts. Fine screw adjustment in thermoregulator operates fully enclosed tungsten contact for fine precision setting (.020F). Bath operating range is ambient to 180°F; can be expanded by addition of special cooling coils for operation below ambient and special heating coils for work above 180°F.

Specially designed mercury relay is built to provide *literally millions* of silent, service-free operations. Controls are installed in compact, self-contained, stainless steel box mounted on aluminum housing. Special stirrer motor, with large air circulating unit on top of motor, cools inside of control box.

T 33700 All-Purpose Economy Bath — complete with heater, heat selection switch, thermoregulator and relay. 115-volt 50-60 cycle A.C. operation. Each **$179.** Entire control unit can be purchased separately.

Write for descriptive bulletin.

GREINER SCIENTIFIC CORPORATION
and Palo Laboratory Supplies, Inc.
22 N. Moore St., Dept. 522, New York 13, N. Y.

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Out of the EDITOR'S BASKET

to 0.1 microgram by means of an optical micrometer scale. This order of readability has never before been attained in an ultra-micro balance with a knife edge beam.

▶ New Gow-Mac solid state dc power supply, Model 405, is redesigned for twice the power of previous models. For complete information readers may request *Bulletin SPPS* from: Gow-Mac Instrument Co., 100 Kings Rd., Madison, New Jersey.

▶ A sighting light called "Site-Lite," which clips directly onto thermometers, burettes, sight glasses, and flowmeters enables the scientist or engineer to make faster, more accurate readings with greater eye comfort. For further information contact, Instruments for Research & Industry, 108 Franklin Ave., Cheltenham, Pennsylvania.

▶ An ultra-micro mull holder developed by Connecticut Instrument Co., Wilton, Connecticut, enables the analyst to easily position microsamples for infrared analysis and to obtain good qualitative spectra without the need of expensive beam condensing optics.

▶ The G-14 graphic recorder now available from Varian Associates, 611 Hansen Way, Palo Alto, California, has a factory-installed integrating attachment that provides a simultaneous measure of the area under the strip chart curve. Useful for many dc recording applications.

▶ A new pump, the "Accu-flo," designed for the precise, reproducible metering of small liquid volumes is announced by Spinco Division of Beckman Instruments, Inc., Palo Alto, California.

▶ The Tecam Sentichart recorder that records minute temperature changes as small as one hundredth of a degree Centigrade can be attached to any oil or water bath. Its temperature span is 0.40 degrees Centigrade, and it operates anywhere in the range from −75 to +175°C. For more information write to LaPine Scientific Co., 6001 S. Knox Ave., Chicago 29, Illinois.

▶ A new electronic null detector suitable for balancing either dc or 60 cycle ac circuits has just been announced by Instruments and Communications, Inc., Wilton, Connecticut.

▶ F & M Scientific Corp., Avondale, Pennsylvania, has announced the availability of a new temperature programmer Model 240M for operation in the range 0 to 1000°C.

▶ A new instrument, the SV2 statistical digital voltmeter, developed by Non-Linear Systems, Inc., Del Mar, California, now makes it possible for an operator to press a button and, within seconds, view

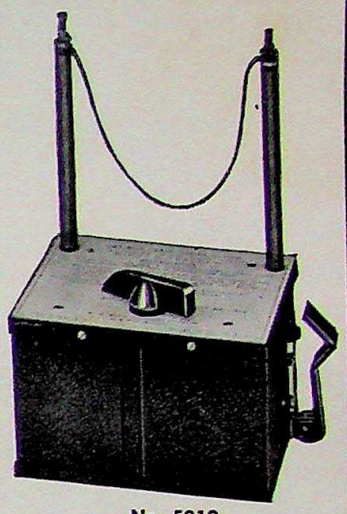
(*Continued on page A204*)

A Laboratory Glass Cutting Unit
Welch HOT-WIRE GLASS-TUBING CUTTER

Produces Clean, Straight Breaks
Cuts Hard or Soft Glass with equal facility

Glass tubing, bottles, or jars up to 3 inches in diameter can be cut neatly and quickly with this cutter. Soft glass, Pyrex-Brand Glass, or other hard-glass tubes can be cut with equal ease. The article is first encircled with a scratch made by a cutter wheel conveniently mounted on the side of the transformer, the scratch is heated by contact with the hot wire, and then cooled quickly by applying water or by blowing on it. No other equipment is required.

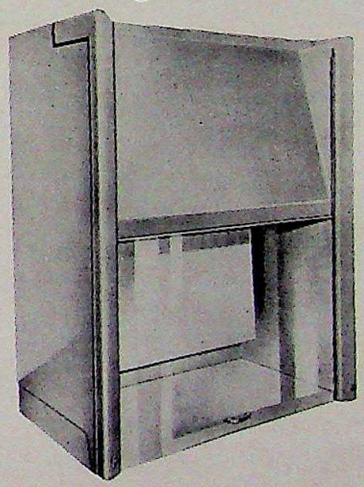
The cutting wire is supported on two insulated posts and is heated by current from a 12-volt transformer serving as the base. No. 24 (B & S gauge) nichrome wire is used and is easily replaced. Three extra wires are included. By means of an adjustment on the transformer, the current can be controlled to give the optimum heat for whatever type of glass may be used. An instruction plate is mounted near this control. The unit operates on 115 volts, 50 or 60 cycle A.C. Over-all dimensions are 6 x 4½ x 9 inches high.



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P-17 Fiberglass VENT ADAPTOR Converts rectangular blower outlet to round opening which will accept stack of 7" O.D..... **$9.75**

RUGGED! Special heat-resistant polyester and fiberglass with smooth, porcelain-like exterior. Resistant to chemical attack. Will not support combustion

HANDSOME! Smooth line design and special finish adds to the general appearance of your laboratory. Thin-wall design adds interior working space.

LIGHT! Superstructure is 47" × 29" × 60" high! Weight with blower only 175 pounds, making it a semiportable unit. Can be mounted on any conventional 47" base cabinet or table, wood or steel.

NON-CLOUDING SASH! Special, clear, resistant coating of ¼" Plexiglass sash prevents clouding. Operates smoothly on fine counterweight system.

QUIET, HIDDEN BLOWER! Powered by ¼ h.p., 115-volt motor, delivers 515 c.f.m. at ¼" s.p. mounted in boxlike rear recess. All wiring to vapor-tight light and to blower molded into hood body and to panel switches.

READY TO USE! Single 6-foot cord and plug connects all electrical equipment to any convenience outlet No electrician necessary. Normally your lab handyman can install it.

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Out of the EDITOR'S BASKET

a statistical graph accurately describing the character of an entire day's production, or a test program, or a scientific experiment.

▶ Hamilton Co., Box 307, Whittier, California, announces successful development of a solid sampler with ease of operation comparable to a syringe. This little-more-than-paper-clip-sized device is of particular benefit to users of chromatographs. Its main feature is a retractable sample tongue within a septum penetrating needle.

▶ A low-cost laboratory chromatograph which will automatically program temperature with reference-column accuracy has been developed by Consolidated Electrodynamics Corp., a subsidiary of Bell & Howell. The programmed temperature range of the Type 26–204 Chromatograph is ambient to 350°C standard; 450°C optional. It can operate in three different temperature modes: (1) programmed, (2) isothermal, and (3) stepwise. Additional data and prices are available from Consolidated Electrodynamics Corp., 360 Sierra Madre Villa, Pasadena, California.

▶ A newly designed automatic balance for general industrial, research and production use has been introduced by the Voland Corp., 27 Centre Ave., New Rochelle, New York. The balance is direct reading —presents an immediate value of weight when a sample is placed on the pan.

▶ New dc differential voltmeter Model 660 has 0.02% limit of error, is stable to 0.01% indefinitely, measures over a 10 microvolt to 5000 v range. Available from Keithley Instruments, 12415 Euclid Ave., Cleveland 6, Ohio.

▶ A new round bottom flask storage rack by Penn-Chem Corp., 232 No. Marshall St., Lancaster, Pennsylvania, provides a maximum of protection in a minimum of storage space. Designed to permit easy, convenient storage of round bottom flasks, the rack contains 22 rings for supporting flasks from 50 to 1000 ml. in size.

▶ A series of new bench-top continuous flow liquid scintillation systems has been introduced by Nuclear-Chicago Corp., 359 E. Howard Ave., Des Plaines, Illinois. These new products, incorporating the exclusive Chroma/Cell flow detector, are designed for measuring the radioactive component of the effluent in a liquid chromatography column.

New Literature

● A single rapid and accurate test with the new Burrell-Severs thermal incline shows the differences in flow properties and setting time of heat-sensitive materials over a wide temperature range. Copies of *Bulletin 335* can be obtained from Burrell Corp., 2223 Fifth Ave., Pittsburgh 19, Pennsylvania.

● LKB Instruments, Inc., 4840 Rugby Ave., Washington 14, D. C., offers *General Catalogue No. 1030E* describing instruments and apparatus for chromatography, conductometry, and electrophoresis.

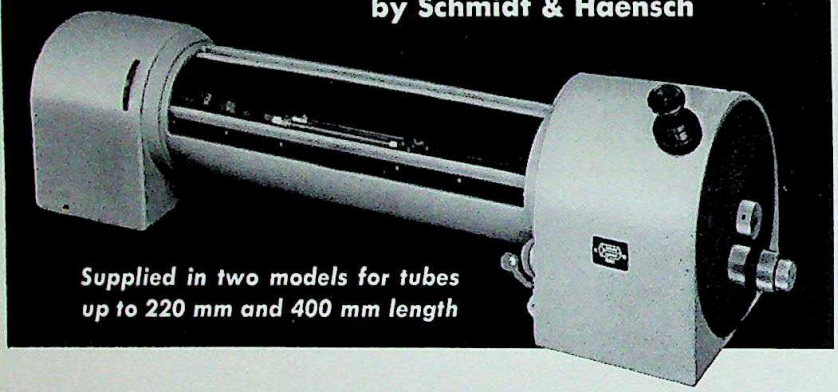
● *Bulletin G-400* describes a modular approach to high performance instrumentation, the GC-2500 gas chromatographs. Write Microtek Instruments, Inc., 550 Oak Villa Blvd., Baton Rouge 15, Louisiana.

● The Radiochemical Division of Nuclear-Chicago Corp., 359 E. Howard Ave., Des Plaines, Illinois, offers a series of new product schedules. These schedules are available on request. Their titles are: Carbon-14 Labelled Compounds; Tritium Labelled Compounds; Phosphorus-32, Sulfur-35, and Chlorine-36 Labelled Compounds; Primary Radioisotopes; Radioactive Standards; Liquid Scintillation Chemicals and Standards; Radionuclides; and Facilities and Services.

● Capabilities of the Type 26-304 moisture monitor are outlined in *Bulletin 26340* from Consolidated Electrodynamics Corp., 360 Sierra Madre Villa, Pasadena, California.

● Copies of *The Struggle for Clean Water* are on sale by the Superintendent of Documents, U. S. Government Printing Office, Washington 25, D. C. PHS Publication No. 958. Price 15 cents. The booklet discusses in detail the causes and effects of water pollution, the technology of water pollution control, and outlines the program to abate water pollution now being carried on by the Public Health Service's Division of Water Supply and Pollution Control.

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FOR BOTH MACRO AND MICRO METHODS

- Direct readings without vernier, with an accuracy of 0.005 circle degrees (estimate 0.0025°) International sugar scale to 0.05°S
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● *Technical Bulletin 114-R* describing the Cary Model 14R recording spectrophotometer is currently being offered by Applied Physics Corp., 2724 Pack Rd., Monrovia, California. The 14R unit is a specially modified Model 14 spectrophotometer for use in the near-infrared analysis of heat-sensitive samples which should not be exposed to undispersed radiation.

● Copies of *Amber-Hi-Lites* No. 70, 71 and 72 may be obtained from Rohm & Haas Co., Resins Department—Ion Exchange, Philadelphia 5, Pennsylvania. These issues describe the use of ion exchange resins in analytical chemistry.

● *Thin-Layer Chromatography—A Comprehensive Bibliography* is compiled, published and available on request from Research Specialties Co., 200 S. Garrard Blvd., Richmond, California.

● A 10 page bulletin, designated *Kem-Kit Bulletin 962*, gives descriptive information on a new line of ground jointed glassware for student use. Featured in this publication are three Kem-Kits complete with molded polystyrene storage cases and student laboratory manuals. Write Kontes Glass Co., Dept. P-126, Vineland, New Jersey.

● Information on six new Pergamon Press, Inc., journals may be obtained from 122 E. 55th St., New York 22, N. Y. They are: *Toxicon*, a quarterly devoted to venoms and poisons; *Neuropharmacology; Medical Electronics and Biological Engineering; Problems of Information Storage and Retrieval and Automatica.*

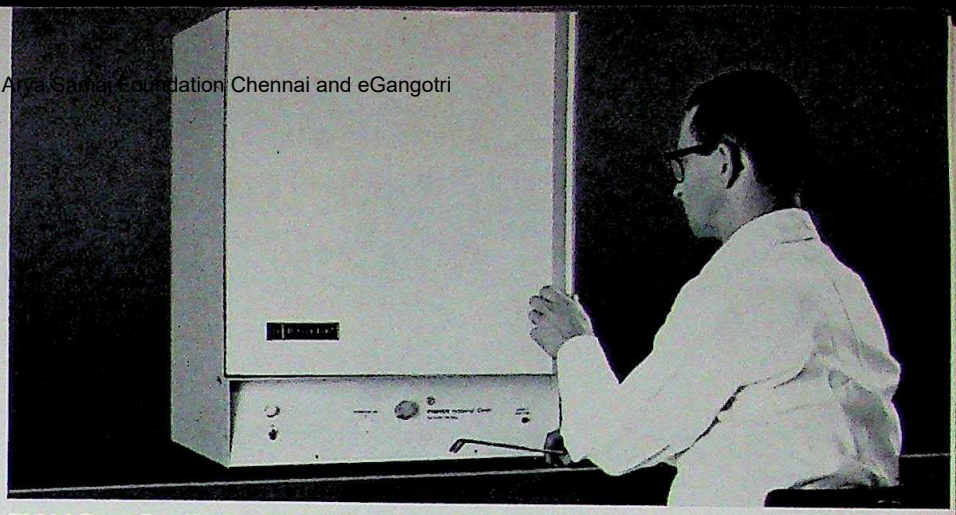
● A number of recently developed methods for the separation and analysis of iodoamino acid in serum and tissue using ion exchange techniques are reported in *Technical Bulletin No. 106* from Bio-Rad Laboratories, 32nd and Griffin Ave. Richmond, California.

● A new illustrated eight page brochure on activation analysis explains this ultra-sensitive analytical technique. Typical applications together with a table of elements and sensitivities are presented. The brochure is available from General Dynamics Corp., General Atomic Division, P. O. Box 608, San Diego 12, California.

● To obtain a copy of the eight-page brochure Bulletin 7009, *The Beckman Ratio Fluorometer*, write to the Scientific and Process Instruments Division, Beckman Instruments, Inc., 2500 Harbor Blvd., Fullerton, California.

● A complete, concise bulletin describes the basic Magnetrol line of liquid level and flow control instruments designed for reliable control of nearly any liquid at

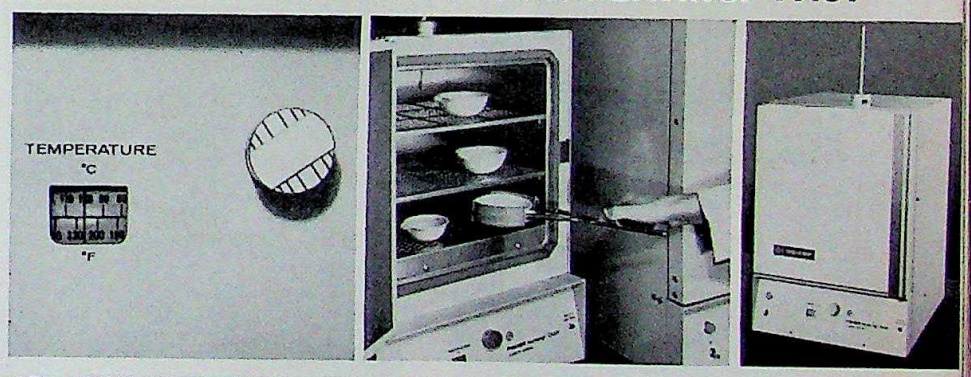
(*Continued on page A206*)



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Out of the EDITOR'S BASKET

practically any pressure or temperature. For a copy of *Bulletin 1A*, write Magnetrol, Inc., 5300 Belmont Rd., Downers Grove, Illinois.

● The Eugene Dietzgen Co, 2425 N. Sheffield Ave., Chicago 14, Illinois, has prepared a comprehensive brochure on their expanded line of graph papers. This six page folder provides a well organized reference, with illustrations in actual color of the 178 different paper available in 80 grid patterns.

● The Bristol Co., Waterbury 20, Connecticut, announces availability of a new 2/10 second dynamaster potentiometer *Bulletin P 1295*. In addition to general specifications and detailed operating characteristics, a four page, full-sized reproduction of an actual chart record is featured.

● Industrial chemicals having applications in 90 S. I. C. industries (U. S. Government Standard Industrial Classification) are factually and interestingly described in The Harshaw Chemical Company's new catalogue, *Chemiscope*, the scope of Harshaw industrial chemicals. Write for a copy, The Harshaw Chemical Co., 1945 E. 97th St., Cleveland 6, Ohio.

● The December issue of the *Gas-Chrom Newsletter* (Applied Science Laboratories, Inc., State College, Pennsylvania) lists several new products not offered elsewhere. This issue includes a bibliography of almost 100 references to gas chromatographic analysis of steroids.

● Order the following, by number, from the OTS, U. S. Department of Commerce, Washington 25, D. C.:

62-11095 *Investigation of the Structure of Metals by Radioactive Isotope Methods*, S. Z. Bokshtein, S. T. Kishkin. L. M. Moroz, State Publishing House, Ministry of Defense Industry, USSR. Moscow. 1959. 205 Pages, Translated for the U. S. Atomic Energy Commission. Three dollars.

NAS-NS-3106 *Paper Chromatographic and Electromigration Techniques in Radiochemistry*. R. A. Bailey, National Academy of Sciences, National Research Council for the U. S. Atomic Energy Commission. June 1962. 48 pages. Fifty cents.

● A 4-page, two-color brochure recently published by Mechrolab, 1063 Linda Vista Ave., Mountain View, California, describes its line of vapor pressure osmometers for extremely rapid and precise determination of number-average molecular weights. The brochure outlines Model 301A's ability to measure a wide variety of samples, and to function with a broad selection of solvents.

● A comprehensive two hundred and forty page multi-color *General Catalogue No. 161* which illustrates and describes Blue M's complete line of electric ovens, furnaces, baths, environmental cabinets, related temperature control equipment and accessories for laboratory, pilot plant and production is now available. This catalogue has a sixteen page Technical Section, compiled to supplement the catalogue descriptions, and a number of scientific charts and tables which will prove to be useful and handy reference material.

Copies of *Catalogue No. 161* are available upon request without cost from Blue M Electric Co., 138th and Chatham Sts., Blue Island, Illinois.

● *Applied Optics*, a publication of the Optical Society of America, has released a supplement on solid state and gaseous optical masers. The *Applied Optics* supplement, which contains general survey articles and important reprints by American, English, French, Russian, and Japanese scientists, reflects the vigorous activity and development taking place in the optical maser field.

There are now optical masers which use many varieties of crystalline material and glasses, and many which use such gases as argon, krypton, and xenon, as well as combinations of helium and neon. Recently the successful operation of a liquid maser was announced.

(Continued on page A208)



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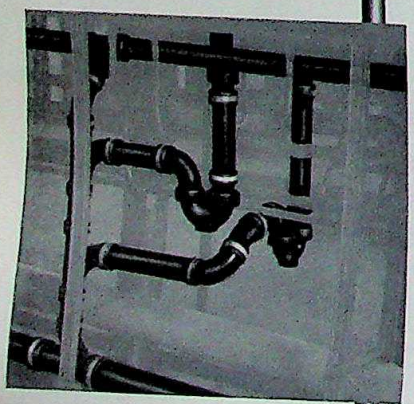
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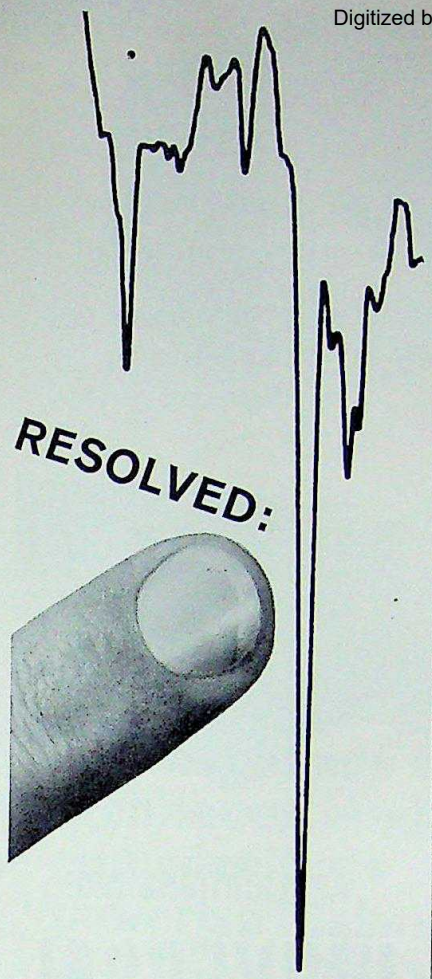
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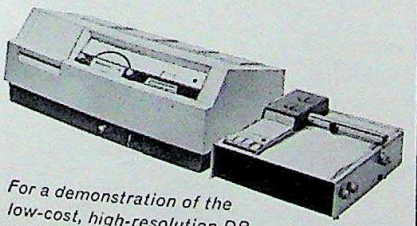
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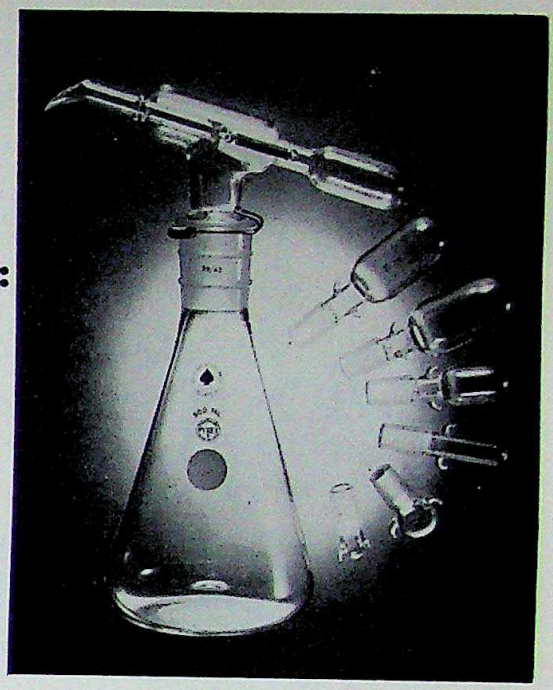
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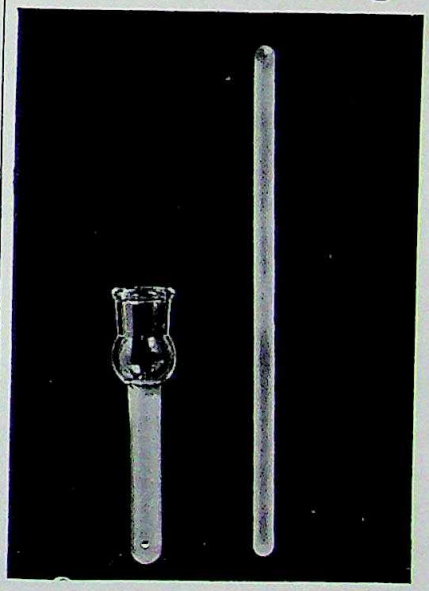
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Out of the EDITOR'S BASKET

Miscellany

★ The role of chemicals in our everyday lives—from the food that we eat to the fuel in our homes and our cars—is detailed in the 5th edition of the *Chemical Industry Facts Book* now available for fifty cents from the Manufacturing Chemists' Association, Inc., 1825 Connecticut Ave., N.W., Washington 9, D. C. A teachers guide to the book will be sent educators using their school letterhead. It provides a list of sources and projects including books, film strips, and motion pictures which augment the information available in *The Chemical Industry Facts Book*.

★ The National Bureau of Standards Student Summer Program for graduate, college, and exceptional high school students interested in science careers was broadened this year to include a series of lectures by President John F. Kennedy and other Federal leaders. The seminars, designed for summer students throughout the Federal service, supplemented their on-the-job experience with an over-all view of Government operations.

The NBS program, which has existed since 1948, has aided the Bureau in its efforts to attract high-caliber young physical scientists and engineers to its laboratories. Students are given an opportunity to apply their education to a challenging summer job and to discover the advantages of a research career at the Bureau. NBS benefits also. Besides contributing to the Bureau's research program during the summer months, many of the students have returned as permanent staff members after graduation.

★ A Summer Conference for College Chemistry Teachers on "Advances in the Chemistry of Coordination Compounds" will be conducted at The Ohio State University from June 17 to June 28, 1963. Thirty stipends of $180 plus travel expenses are available for college and university teachers of inorganic chemistry. The Conference program is composed of an intensive two-week lecture course on modern coordination chemistry. The course has been organized and will be presented, in part, by the members of the Division of Inorganic Chemistry, The Ohio State University.

Applications and inquiries should be directed before April 10 to: Prof. Devon W. Meek, Department of Chemistry, The Ohio State University, 88 W. 18th Ave., Columbus 10, Ohio.

★ University of Southern California is pleased to announce the 1963 seventh annual Continental Oil Company Contest in Colloid and Surface Chemistry for college undergraduates. Information and contest rules are available from the contest chairman: Robert D. Vold, Department of Chemistry, University of Southern California, Los Angeles 7, California.

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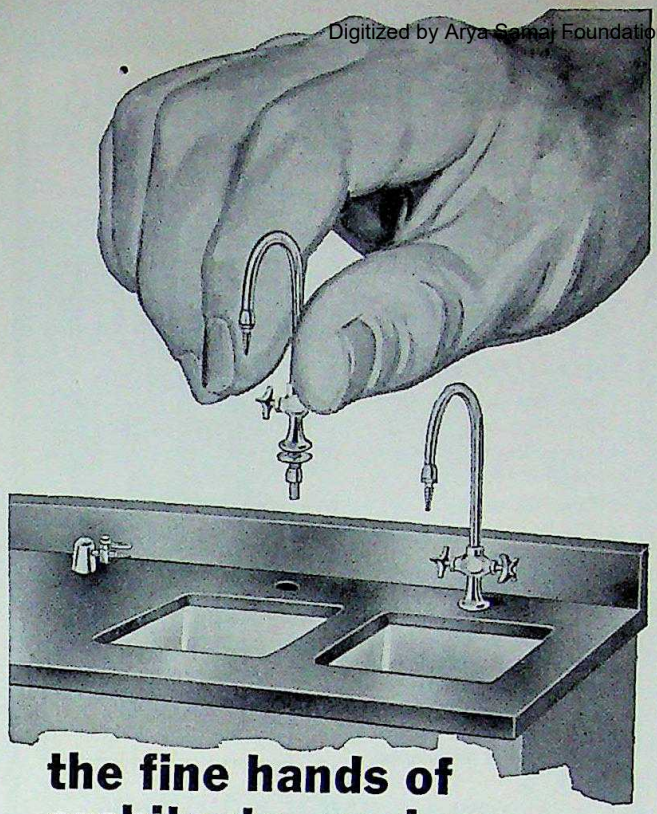
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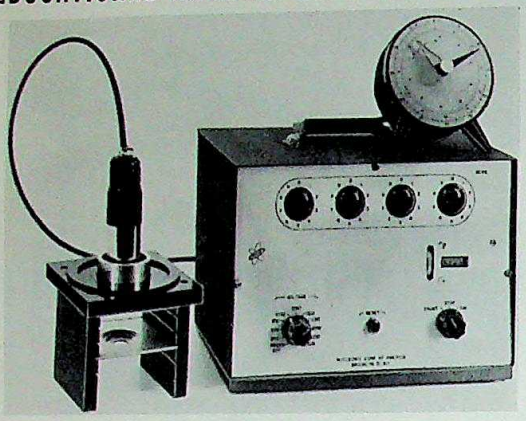
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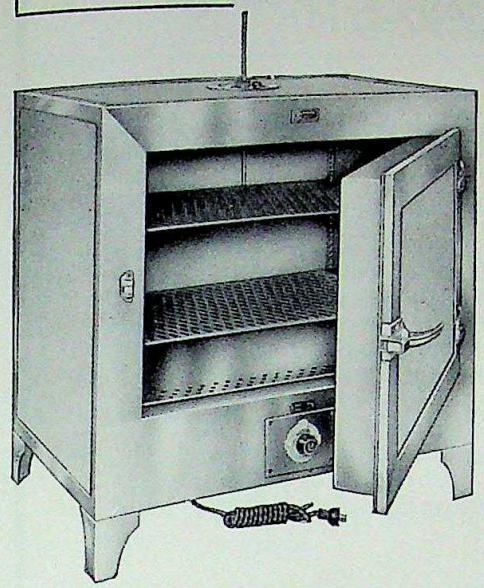


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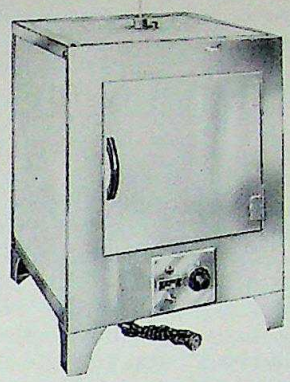
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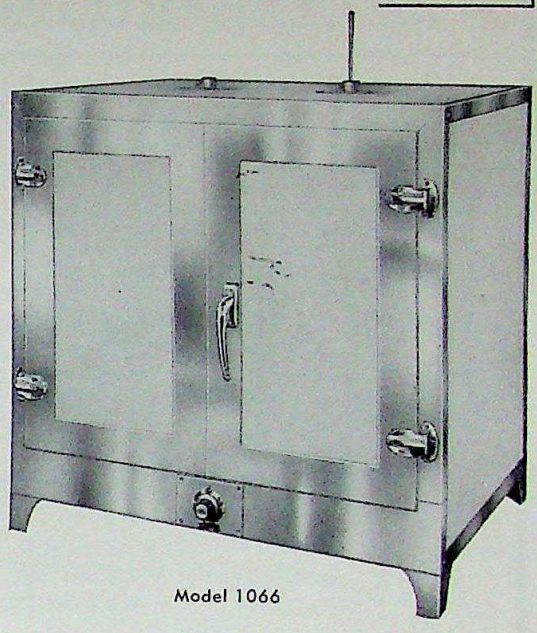
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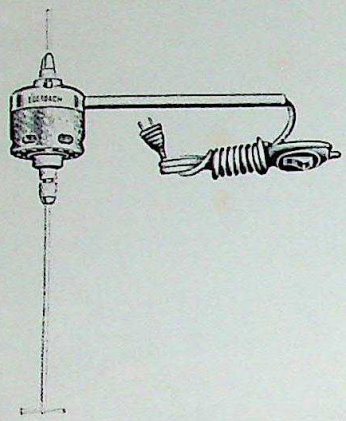
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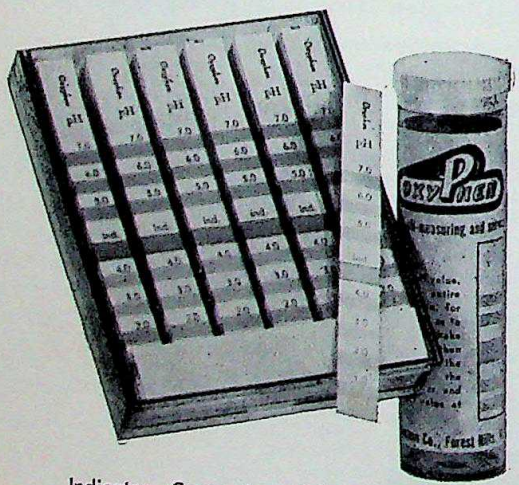
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2. OXYGEN

D. Some Oxidations *(continued)*

3. OTHER COMBUSTION PHENOMENA

Dem. 62—Dust Explosion

To show: The effect of area exposed to reaction on rate of reaction.

Materials: Lycopodium, eye-dropper, alcohol burner.

Procedure: Place the lighted burner on the stage and project. Suck up half a dropperful of lycopodium (it sucks up just like a liquid) and squirt into the flame. Repeat on the lecture table.

Observation: The sudden flare as the dust explodes is more dramatic on the table top. However, it is also instructive to see the action amplified on the screen.

NOTES: 1. Flour can be used in place of lycopodium powder, but must be thoroughly dry. Heat the flour to drive off the moisture, then place it at once in a tightly-stoppered bottle until use.

2. Teachers may prefer to demonstrate the dust explosion using the macro-techniques described in the Tested Demonstration Series, *J. Chem. Educ.*, **32**, 15 (1955), Figure 2–17. If so, it is well to construct a transparent, 4 1/2-inch high working model and project its operation before carrying out the macro-explosion. Follow Figure 2–17 in constructing the model. Make the sides of the model flat and parallel for clear projection. Lead a 4 mm. o.d. vinyl tubing into the shoulder of the plastic model, having curved the other end and flared it into a funnel after warming to soften it. Replace the rubber aspirator with the bulb from a medicine dropper. Use a 2-inch birthday candle stuck into wax on the bottom of the model can. Place on the stage and project, explaining its parts and operation. Introduce the lycopodium from a medicine dropper lowered into the model. Use a taper to light the candle. Cap the model with a rubber cap similar to those used on the culture tubes. To demonstrate what occurs in the 3-gallon milk-can explosion, squeeze the rubber bulb to expel the lycopodium from the funnel; it is not essential that an actual explosion occurs. Then repeat the demonstration on the macro-scale using the 3-gallon milk can device, Figure 2–17.

Dem. 63—Ozone Formation and Reactions

See Special Devices SD-9. This is a flow-type ozonizer. It is used to (*a*) color starch-iodide solution blue, (*b*) liberate iodine from KI-aq., the I_2 being concentrated in CS_2.

E. Ozone

Dem. 64—Ozone Formation in Silent Discharge

See Special Device SD-10. This is a static device which can be used both as an ozonizer and as a Cottrell Precipitator.

SUPPLEMENTARY DEVICES

SD-9—Flow-Type Ozonizer

Construction of SD-9: The device shown in Figure SD-9 is made of plastic; dimensions are not critical. The delivery tube is fixed in place and leads into the reaction box, which is also cemented in place. If the end of the delivery tube is cut on the bias, bubbles escape smoothly. The generator tube is filled loosely with steel wool.

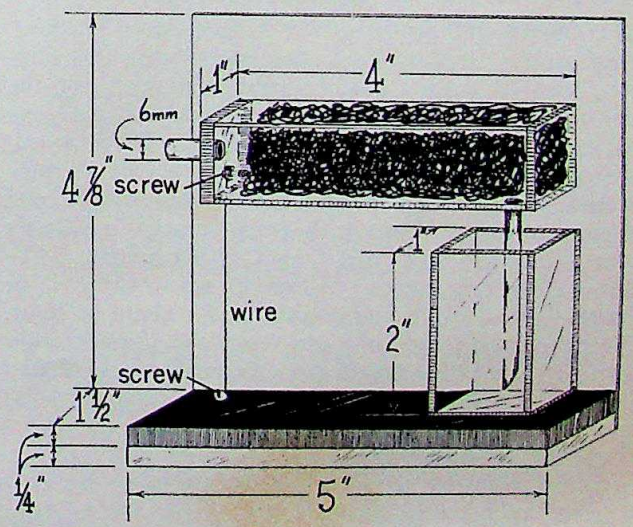
To show: The preparation and reactions of ozone.

Materials: SD-9, KI-aq., CS_2, KI-starch solution, Tesla coil leak-tester, oxygen.

Procedure: (*a*) Fill the reaction box two-thirds full of KI-starch solution. Place on stage and project. Pass a lively stream of oxygen through the steel wool and reactant solution. Now bring the leak-tester to the tube containing the steel wool so that the arc sprays over the tube into the steel wool to the gounding nut. (*b*) Repeat using KI-aq. in the reactor box; then add a 1/2-in. layer of CS_2 and swirl.

Observations: (*a*) Over 1% ozone is produced; it immediately colors the starch-iodide solution deep purple. (*b*) In the absence of starch, the iodine which is released gives a slight brown coloration to the solution. Upon adding the CS_2 the iodine collects as a purple layer at the bottom of the box. (Rinse out at once.)

Reference: WORSTELL, R. A., *J. Chem. Educ.*, **9**, 291 (1932); RANSFORD, J. E., 28, 477 (1955).



SD-9 FlowType Ozonizer

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This device was developed by Roger Hanson and his teacher Mr. Melvin E. Olene of Highline High School, Seattle, Washington working with the author at the Science Theater Laboratory, U. S. Science Exhibit, Century-21, Seattle, Washington, 1962.

Construction of SD-10: The metal strip and wire screen are bolted to the $5 \times {}^{3}/_{4} \times {}^{1}/_{8}$-in. plastic strip as shown in Figure SD-10. Two different styles of electrodes are prescribed so that during projection it emphasizes that they are of different charge, thereby attracting the charged colloidal smoke particles differently. The electrodes fit into the standard reaction cell C-1.

Use as a Cottrell Precipitator

To show: The removal of smoke by electric discharge.

Materials: SD-10, cigarette or conc. NH_4OH + conc. HCl as a source of smoke, Telsa coil leak-tester, cell C-1.

Procedure: Fill cell C-1 so completely with smoke that the cell appears opaque when placed on the projector. The smoke can be blown in from a cigarette, or it can be NH_4Cl made chemically by holding over cell C-1 the mouths of bottles of conc. HCl and conc. NH_4OH. Project. Now bring the leak-tester to one electrode.

Observation: A swirling of smoke commences immediately, and the smoke is deposited out on one of the electrodes only.

Use as an Ozonizer

To show: The production of ozone by sparking in air.

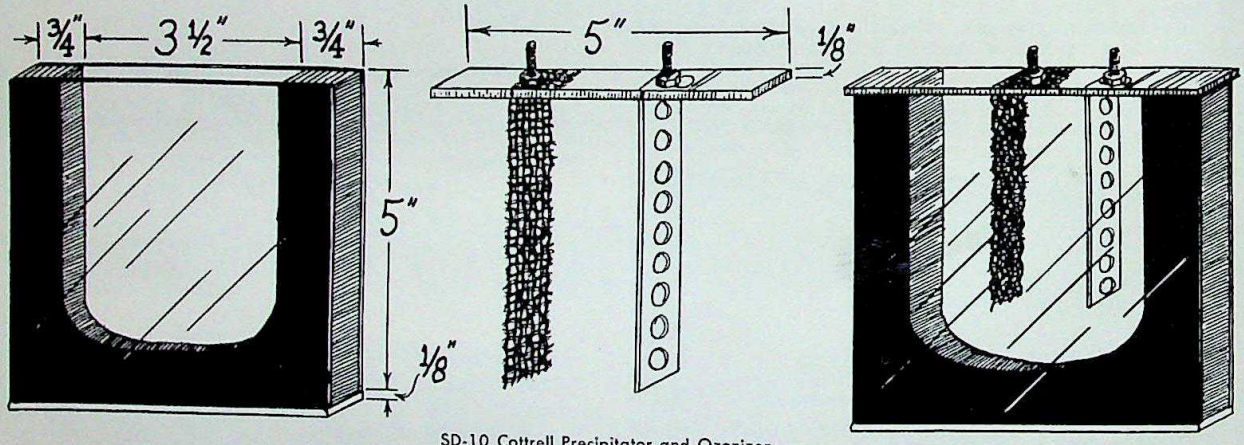
Materials: SD-10, KI-starch solution, Telsa coil leak tester, C-1, a foot of bare copper wire about No. 24.

Procedure: Poke one end of the copper wire into cell C-1 so it reaches to the bottom of the cell; ground the other end by fastening it to some part of the projector. Now into cell C-1 pour KI-starch solution so it is just below the two electrodes of SD-10. Project. (*a*) Bring the leak-tester to one electrode. (*b*) Pass the cell around the class.

Observation: (*a*) Ozone is produced, and the solution just below one of the electrodes can be seen swirling and turning blue. (*b*) The odor of ozone can be easily detected as the cell is passed around the class. Discharging the leak-tester directly into the grounded cell will also produce ozone, but the use of SD-10 improves the effect.

Note: A screw can be inserted in the base of C-1 to give permanent ground.

References: Doane, H. C., *J. Chem. Educ.*, **9**, 1113 (1932); Lisk, G. M., *ibid.*, **9**, 2099 (1932).



SD-10 Cottrell Precipitator and Ozonizer

SD-11 Silicone Rubber Stoppers

Mr. Charles W. Owens of the N.R. Crozier Technical High School, Dallas, Texas has contributed the valuable idea of casting silicone rubber stoppers for the culture tubes used in TOPS devices, and sent me some excellent samples. His recipe follows. Drive a nail through a board, turn the board over and over the projecting nail place a 3-inch section of culture tube, and cement it to the board with Duco cement or Elmer's glue. Into the tube pack Dow Corning Silastic RTV-521 and curing agent. Allow to set overnight, or hasten curing by placing in an oven for about an hour. Now break open the tube and remove the silicone rubber. Cut it into slices for one-holed stoppers. Two nails will make two-holed stoppers; no nail, solid stoppers.

Acting on Mr. Owens idea we have made silicone rubber stoppers using General Electric RTV-60 silicone rubber and curing agent. Pack the mixture into a culture tube. Allow to cure at room temperature for forty-eight hours. Now cut the glass tube on a diamond saw into ${}^{3}/_{4}$-inch sections, and push out six silicone stoppers. Holes may be bored in these as with rubber stoppers.

Correction

Demonstration 4. Iron, Sulfur and Iron Sulfide. Do not use this as an example of stoichiometric combination. I am indebted to *Dr. Allan Adair of Kelly College, Devon, England,* who has called my attention to a report by Bernal, J. D. and Crowfoot, D. M., *Annual Reports, Chem. Soc., London,* **30,** 385 (1933) where they state that "the stoichiometric compound FeO or FeS cannot be formed at all, in spite of the assurance of elementary chemical text books. The lattice shrinks as the iron content is reduced, which is consistent with the theory that it consists of an ideal lattice FeO, FeS or FeSe, with an increasing number of iron atoms removed, leaving spaces which are partially filled by adjustments of the other atoms. . . . . The necessity of considering these non-Daltonian or Berthollide compounds [a term first introduced by Kurnakow, *Z. anorg. Chem.*, **88,** 109 (1914)] in relation to the ordinary conceptions and notations of chemistry is becoming increasingly urgent, as most metallic and sub-metallic (sulphide) systems are essentially of this type, as well as many ionic and molecular compounds. Various references are given. Hägg studied the Fe-S system, *Z. physikal. Chem.* [B], **22,** 453[1933]; *Nature,* **131,** 167[1933]; A342.

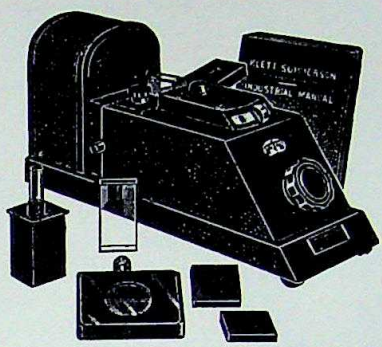
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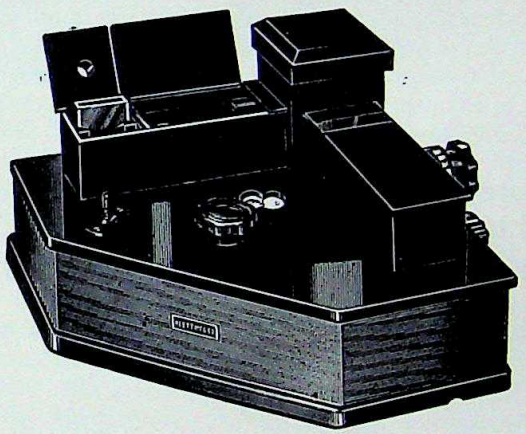
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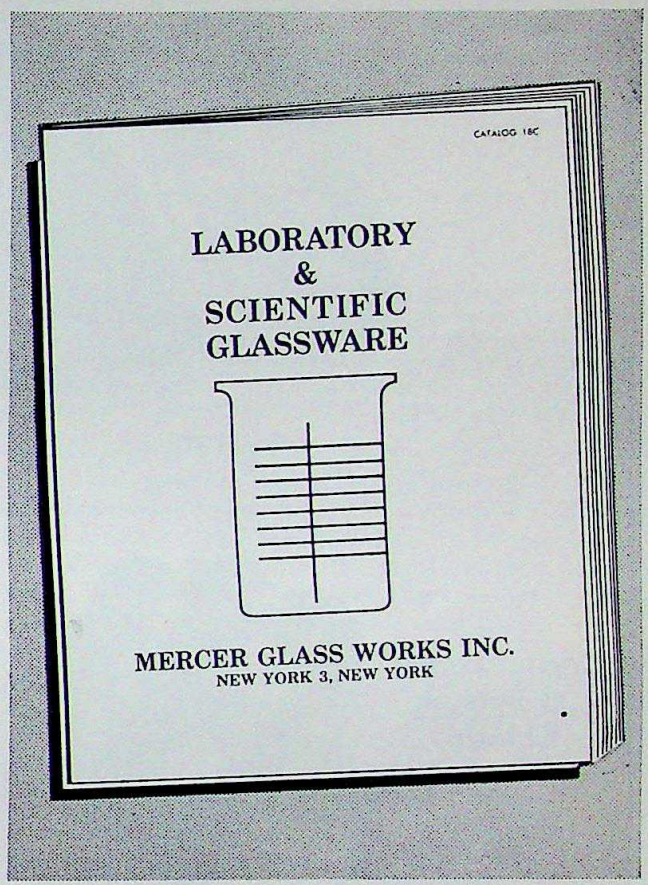
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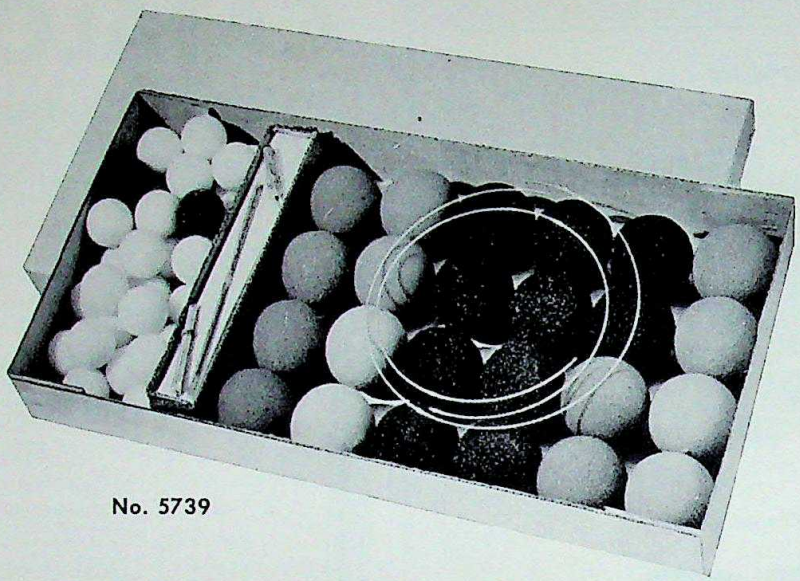
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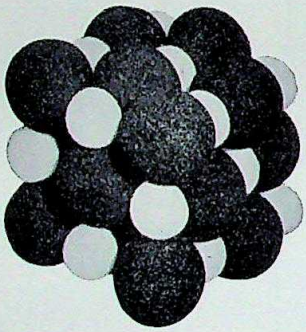
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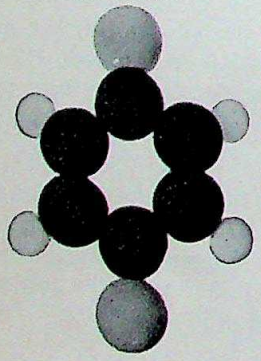
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EDITORIALLY SPEAKING

The "Tyranny of Testing" is the frightening title of a provocative book by Banesh Hoffman, published by Crowell-Collier Press (1962). All educators, from a graduate assistant making up his first quiz to school superintendents and university presidents designing educational policy, should read this thoughtful, if acidulous, attack on a phenomenon of our time, the multiple-choice examination. Dr. Hoffmann has consolidated into one book his attack begun in numerous essays which have appeared during recent years in such periodicals as *Harper's Magazine*. These initial skirmishes often were so taunting that the reaction of the testing industry resembled a chip on its shoulder. In this volume, Dr. Hoffmann unequivocally knocks off the chip. The story of the scrap is good reading. Incisive thinking, described in delightful prose is persuasive indeed, especially when the opponent is cast as a big bully supported by the intimidated or, at best, uncritical crowd.

Dr. Hoffmann's persuasiveness needs no assist here. He uses such chapter titles as "David and Goliath" and "Don't Pro-Test—Protest" with effectiveness. Readers of these pages need not be urged to regard excessive or exclusive use of multiple choice "objective" tests as dangerous. They view with equal alarm, ". . .the characteristic chain which begins with method and ends with gadgetry." They shout with equal resentment at the twisted semantics which use the word, *scientific*, as "an article of faith among statistically minded objective testers." We expect that readers use well constructed, standardized—yes, even "multiple-choice"—tests with full realization of their limitations as well as their unique advantages. We do not advocate a complete banishment of them from the chemistry classroom.

Our purpose here, rather, is to urge every amateur test writer (and what teacher can ever claim other than amateur status!) to realize how often an examination question traps the tester instead of the testee. A few pertinent quotations drive home the point:

> . . .The term "objective" test is a misnomer. The objectivity resides not in the test as a whole but merely in the fact that no subjective element enters the *process* of grading once the key is decided upon.

This is a sobering thought to start with. Though we gladly feed the student's answer to an I.B.M. machine, do we really want him merely to consult his own mental I.B.M. machine to answer the question? Our expectations of his speed of response implied by the number of questions presented in a given time also may reflect our faith in the student's "objective" (machine-like) mental machinery.

> . . .The tests deny the creative person a significant opportunity to demonstrate his creativity and favor the shrewd and facile candidate over the one who has nothing of his own to say. . . . They penalize the candidate who perceives subtle points unnoticed by less able people, including the test makers. . . . Questions are made artificially difficult by means of ambiguity.

Ambiguity is a nasty word when applied to an examination question where no opportunity is given for statements of reasoning behind an answer. Often the questioner dodges his responsibility by asking not for the correct answer, but the "best" answer. Chemists grin complacently when they hear the apocryphal story of the true-false economics examination which was useful even after thirty years in fraternity files because the answers were different then! Yet at the same time these chemists insist on asking similarly for a "best" answer, even to a question made more uncertain by being a "because" question. Dr. Hoffmann has a most enlightening time with the following:

> Potassium metal loses electrons when struck by light (the photoelectric effect) more readily than lithium metal because
> (A) the potassium atom contains more protons than does that of lithium
> (B) the valence electron of potassium is farther from the nucleus than is that of lithium
> (C) potassium occurs above lithium in the electrochemical series
> (D) the potassium atom contains more electrons than does that of lithium
> (E) the potassium nucleus is larger than that of lithium

Since the more immediate "cause"—the difference in energy required—is not among the choices, we venture to guess that readers who probe beneath their first reaction will be able to see justification for all answers except C.

We recall a story that has stuck with us since the days of the radio "Information Please" program. The question asked was, "If the sun should suddenly stop shining on China, could a boy kiss his girl in the moonlight in America?" The anticipated response was "No," the obvious reasoning being that the sun is responsible for the moonlight. A high school general science student, however, answered "Yes." He pointed out that since light travels at 186,000 mi/sec, the astronomical and biological facts of life would allow adequate though somewhat less than satisfactory time, 2.6 seconds.

Could an I.B.M. machine handle that answer and keep its fuses intact?

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Henry M. Leicester
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Some Aspects of the History of Chemistry in Russia

A consideration of the history of chemistry in Russia as an example of the general attitude of Russia toward science can be very instructive, both by explaining some of the features of Soviet science which have often puzzled Western observers and by indicating some of the possibilities for science in general which could ensue as a result of present policies in the modern world. This paper will attempt to develop a few of these points.

Probably the chief difference between the development of science in Western Europe and in Russia at the beginning of the eighteenth century[1] lay in the fact that Western science had grown gradually and naturally, arising from the mingling of many cultural streams, and was firmly based in the technical and intellectual lives of the people among whom it arose. In Russia, on the other hand, no such gradual development had occurred. There had been a technological expansion—in the manufacture of drugs, gunpowder, and assaying techniques—which was essentially the same as that of western Europe at the same period. This is not strange, for the technical processes were carried out almost exclusively by western artisans, imported for the purpose. Native Russians seldom had the training to carry on these processes. In the intellectual life of the highly stratified Russian society there was no interest in scientific problems, and very little even in the applications of science.

Thus when Peter the Great in 1724 decided that he could further his projects for the westernization of his country by creating an Academy of Sciences on the French model, he was forced to staff it entirely with foreigners brought to his new capital of St. Petersburg and given substantial material inducements to draw them to this raw, new city.

Science was thus imposed upon Russia by outsiders, just as technology had been. This characteristic domination of early Russian science by foreigners who acquired a vested interest in maintaining their special privileges was so strong that when a truly Russian scientific genius did appear in the person of Mikhail Vasil'evich Lomonosov (1711–65),[2] he was unable to exert an influence equal to his abilities on the scientific world of his time. Although his views on chemistry, physics, technology, and many other scientific fields were far in advance of his day, he was prevented from applying them to the full, largely because of his constant quarrels with his German colleagues in the Academy of Sciences. Most of his important work remained unpublished and unknown to the scientific world. It was only in his poetry that he was relatively free to express himself; and so, for nearly two hundred years he was

[1] LEICESTER, H. M., J. CHEM. EDUC., 24, 438 (1947).
[2] FARBER, E., edit., "Great Chemists," Interscience, New York, 1961, pp. 201–210.



Mr. Joseph Evans, Vice-president Dexter Chemical Corp., Dr. Leicester, and Prof. Aaron J. Ihde, Chairman Division of Chemistry

The 1962 Dexter Award winner, Henry M. Leicester, long has been a friend to readers of THIS JOURNAL. Two editors have sought his advise and counsel; for a decade (1949–59) he was a member of the Editorial Board. Numerous articles have come from his prolific pen. He also served as editor and contributor to the sixth edition of Mary Elvira Weeks' classic "Discovery of the Elements."

Prof. Leicester since 1950 has been the head of the Department of Physiological Sciences, College of Physicians and Surgeons of San Franciso. In addition to being a historian, he is a well-known biochemist contributing to an understanding of the chemistry of teeth.

His writings on Russian chemistry include works on Butlerov, Zinin, Markovnikov, Lowitz, Blokh, Mendeleev, and "The History of Chemistry in Russia prior to 1900." Through his knowledge of the Russian language and his personal contacts with Russian historians of science, Prof. Leicester has been responsible for drawing them closer to American historians of science.

Dr. Leicester received AB, MA, and PhD degrees in chemistry from Stanford University. He was one of the founders of *Chymia*, The International Journal of the History of Chemistry, and is presently its Editor-in-chief.

The Dexter Award includes a $1000 prize and a plaque. Previous winners of this award are: 1956, Ralph E. Oesper; 1957, Williams Haynes; 1958, Eva V. Armstrong; 1959, John Read (Great Britain); 1960, Denis I. Duveen; and 1961, James R. Partington (Great Britain).

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known chiefly as a poet rather than as a scientist. It can be seen that even a man of undoubted genius cannot be effective when the atmosphere surrounding him is unfavorable.

Following his death, native Russian science languished, and only foreigners carried on the work of the Academy. This was an undistinguished period in the history of Russian science.

At the beginning of the nineteenth century a new wave of westernization swept over Russia and resulted in the foundation of a number of provincial universities. Here for the first time it became possible for young Russians to study the science of the West. At first progress was slow, since this new generation was only beginning to learn the actual conduct of research. As these men matured, however, and taught the next generation the ideas they had absorbed, the methods of western science spread through the universities; and research in the Western sense began to be carried out. Thus, for example, after 1830 the University of Kazan was a major center of chemical activity which for a time exceeded any activity at the Academy of Sciences, and where research was carried on by native Russian scholars.

This scientific research was, however, not completely free. The Russian universities were controlled by the government and a close watch was kept on the teachings of the professors. Too liberal ideas among the faculties or student bodies could result in closing the universities, sometimes for long periods. Especially in the later years of the nineteenth century, student riots and closed universities were quite common. Nevertheless the scientific fields were not as suspect as those subjects more closely related to politics and economics. The scientists were left to themselves, so long as they worked in scientific fields only. As a result, a true Russian science grew up, practiced by Russians in their own country and firmly based in the intellectual life of the nation. Thus science reached its highest point, at least in chemistry, in the years between 1840 and 1880—names such as Markovnikov, Butlerov, and Mendeleev stand out in the history of world chemistry..

The increasingly tense political situation after the assassination of Alexander II in 1881 resulted in more restrictive measures against even scientists, and both Markovnikov and Mendeleev, in spite of their scientific eminence, lost their university professorships because of their liberal political ideas. The succeeding generation of scientists, with few exceptions, did not measure up to the achievements of their predecessors.

This brief survey of the history of chemisty in Russia indicates quite clearly that, in order to achieve its greatest progress in a nation, a science must be firmly based in the life of that nation. Thus, the solid foundation of science in the culture of Western Europe certainly helps to account for the outstanding progress which it made after the Renaissance. The progress of Russian chemistry was marked, not when one genius attempted to further it but when it became part of the intellectual life of the nation, even though this intellectual life may have been but a small fraction of the total culture of that huge country.

Some further conclusions of interest can be drawn from the history of chemistry in Russia. It was formerly thought by many Westerners that Russia was a backward country intellectually, and that her science and technology were taken almost entirely from foreign sources. The spectacular advances in space research in the last few years startled those who held this view, but not those who were familiar with history. There had been no doubt as to the originality and ability of Russian scientists after the nineteenth century. At the same time, a knowledge of Russian history also helps to explain some of the other puzzling and contradictory features of present day Soviet science. Actually neither the ability shown by the space scientists nor the excesses of Lysenkoism and the rejection of the resonance theory should be surprising. Both aspects are a continuation of tendencies which have long been present.

Throughout its development, Russian science was regarded with mixed emotions by the governing class. As shown, science was never completely free from governmental supervision, and the supervisors always showed curiously ambivalent attitude in their work. The Czar might personally recognize the value of Mendeleev, the scientist[3]; but Mendeleev, the liberal, could never gain admittance to the Academy of Sciences,[4] which was controlled by the politically powerful and conservative German party. Thus he could be summarily dismissed from his university position when he supported the liberal views of some of the students. This distrusting of the scientist while at the same time valuing his work is not, perhaps, confined to Russia; but it was very pronounced there; and it may have been augmented because of the imposed character of Russian science in its early days. It seems to have been a continuous feature of Russian scientific life at all times.

When the tremendous expansion of scientific activity took place after the Revolution, this attitude did not change. The need for science was now even more obvious to the politicians, but the suspicion of it continued. It was probably intensified by the defection of such prominent chemists as Chichibabin and Ipatiev after World War I. Thus it was felt to be necessary that the scientist conform to the dominant ideology of the government before he could continue his work, just as had been the case in czarist Russia.

The scale of science in the Soviet Union today is vastly greater than it has ever been, but its roots lie in the past, and this must be considered in any evaluation of the present position or the future prospects. The study of the history of Russian science is as essential to an understanding of the Soviet Union as is any study of her political and economic policies.

[3] Farber, E., *ibid.*, pp. 719–32.

[4] Leicester, H. M., J. Chem. Educ., **25**, 439 (1948).

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Amos G. Horney
Air Force Office
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Washington, D. C.

Proposals for Significant Research in Chemistry

Many investigators with significant research ideas find it necessary to seek supporting funds from agencies outside of their own. A high proportion of available funds for this purpose is obtainable through many of the various Federal agencies.

The usual method of obtaining funds from such agencies is a request in the form of a research proposal. Although each agency has its special interests, suggested formats and its own mode of selecting the research which it will support, there is also much in common among them. In fact, representatives of the various Federal agencies supporting basic chemical research have informal meetings twice a year to discuss policy, procedures and problems of mutual interest. These agencies also frequently exchange lists of official proposals.

The purpose of this paper is to give the reader an insight into the special interests and mode of selection used by one of these Federal agencies—namely, the Directorate of Chemical Sciences, Air Force Office of Scientific Research (AFOSR). The use of this information in preparing a proposal may increase the reader's chances of obtaining support from any agency. Here, however, is an example of a proposal received within the government some time ago which probably did not receive support. Details are left to the imagination of the reviewer: "United States Government, Attn.: President Dwight D. Eisenhower: We are seeking finance to build equipment for space rockets. Our estimate is for a request of $8,000,000 now. Thank you in advance. Very truly yours, Signed. . . ."

Research proposal requests successful in obtaining funds from AFOSR, Chemistry, generally have gone through three steps: (1) a review of a preliminary proposal, (2) a review and evaluation of an official proposal, (3) a final evaluation in terms of funds available. Case histories of proposals going through these steps will be given after a preliminary discussion of the nature of the "new science" which AFOSR seeks to support through its Directorate of Chemical Sciences.

In a military sense the ability to prevail is directly related to the technologies of the day. These were spawned by the science of a previous day. The science of today and the "new science" of tomorrow are the indispensable foundations for the revolutionary weapons of the future. The Air Force draws upon a large per cent of our total national resources, including our national reservoir of scientific knowledge. Therefore, the Air Force must put at least a minute portion of its funds into creating new science.

The mission of the Directorate of Chemical Sciences is to promote the creation of new chemical areas on the frontiers of known science. How is this done? It is done primarily by *selecting* investigators through their research proposals which have been submitted for consideration, and then *encouraging* them with funds and by other means.

Proposal Case Histories

In response to inquiries for an expression of AFOSR research interests, a list of researches assisted by the Chemical Sciences Directorate and a "guide" for preparing preliminary proposals are sent to the questioner. With a slight modification here is a quotation from that guide:

> The Air Force Office of Scientific Research can accept only *unsolicited original* proposals for basic research. AFOSR is not interested in telling investigators what they should do, for the best ideas originate in the minds of the men actually involved in research. Our primary interest is in the ability of the investigators and in their research preferences. Contrary to the expectations of some, AFOSR seeks originality and novelty of approach—does not automatically decline the unconventional. If our philosophy were to be summed up in one sentence it would be: 'If you are seeking predictable results, it is not basic research.' AFOSR may best learn of your interests by a letter or a brief. An elaborate presentation is not desirable; however, good science is required.

The selection process is carried out, as previously mentioned, in three steps:

Informal Proposal

Step 1. The investigator himself generally submits an informal proposal outlining a four-year program, stating his research objectives, the scientific significance of his objectives, his specific plans for starting and the approximate cost for each of the first two years. The informal proposal is given immediate staff review. Please note why Dr. A is unsuccessful in the *first case* as staff comments are quoted:

> Good exploratory but not basic research . . . others are doing this kind of thing and have been for some time . . . reasonable objectives, old approach . . . some of the species mentioned are interesting but the objective seems to be more technique perfection than gathering new knowledge. . . . This is just an exploration of some cryogenic techniques which will probably not give anything new to the principles of chemistry. . . . Dr. A might find something about properties of the molecules cited, but his objectives do not seem to include new fundamental understanding.

In a letter mailed in less than two weeks after his informal proposal was received, Dr. A was told that his proposal seemed insufficiently competitive, when

This article is based on a paper given before a joint session of the Divisions of Petroleum Chemistry and Chemical Education at the 141st Meeting of the American Chemical Society, Washington, D. C., March, 1962.

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considered along with many others, to make it worth while for him to take the time and trouble to prepare an official one.

Official Proposal

Step 2. In a *second case* Dr. B submitted an informal proposal which in the staff opinion warranted more extensive review. Dr. B was informed by letter that an official proposal was welcome but the competition for available funds was keen. The formal proposal was received and acknowledged, and the investigator advised that technical evaluation would take approximately three months. It was submitted for final evaluation and then discussed by the reviewers in one of our semiannual committee sessions. As I quote remarks from the final evaluation, note why Dr. B was unsuccessful: One reviewer said:

> The proposal from Dr. B has been carefully prepared . . . proposes a general reinvestigation of all the chemistry of X . . . However, I was unfavorably impressed by several items in the proposal. (1) The structure of the X Grignard is discussed, as if it were possible to determine the structure of a compound in mobile chemical equilibrium by chemical means. Perhaps the structure is not important; perhaps only the reactions are significant. But if one wishes to find the structure, it must be done by physical measurements, e.g., by NMR spectroscopy, following the methods published by J. D. Roberts. (2) The mechanism for the alkylation of X with Y seems unrealistic. The authors ought at least to have considered the possibility of an oxidation reduction chain, with attack on the X by an aldehyde obtained by dehydrogenation of the alcohol. These examples suggest to me that Dr. B is more ambitious than skilled.

Regarding Dr. B's proposal another reviewer remarked:

> Am I perhaps unjustly suspicious of a proposal which (a) tries to entice the interest of the Air Force by listing as potential uses of chemistry part of the subject index of *Chemical Abstracts*, and (b) outlines as a serious investigation for three people (with the principal investigator giving only 25% of his time) a lifetime project in X chemistry? I am particularly disturbed by an apparent unfamiliarity with previous work in X chemistry—to cite only two examples, both the nitrosation of X and studies on its role in the Diels-Alder reaction have been studied, but no references are given. Perhaps more disturbing is the failure to mention Dr. M's work on the alkylation reaction with alkoxides. This proposal is too broad, amorphous, unrealistic, and uninformed.

A letter expressing sincere regrets to Dr. B, two months after receipt of his official proposal, stated that it was not sufficiently competitive with the many fine proposals under consideration for his research to be included with funds available.

Third case: In January, 1959, Dr. C inquired whether AFOSR had an interest in a new inorganic polymer. In response to his inquiry Dr. C was told yes, if the idea was new and gave promise of opening up a new area of chemistry. On the other hand, if it was an idea similar to the extensive program being carried out by other agencies or was not different in approach from the large program sponsored by others, the answer would be no.

Dr. C's preliminary proposal was received. He outlined a four-year investigation with a cost estimate for each of the first two years. Then, after receiving an encouraging response, he submitted an official proposal through his University channels. I now call your attention to the character of the remarks made by our evaluators. One said:

> Dr. C is a young man well thought of by his colleagues . . . his proposal concerns new work . . . the field is thoroughly interesting. . . . I am confident that a lot of nice new inorganic chemistry will come out of this . . . even though he casts his discussion in terms of polymers.

Another reviewer said:

> The proposal is clear, interesting . . . should yield interesting information . . . claim of polymers of high thermal and chemical stability . . . is justified . . . field intriguing . . . investigator qualified . . . budget reasonable.

Assignment of Priority

Step 3. Our staff prepared briefs of the proposals received from Dr. B and Dr. C and briefs of the evaluations. These, along with others, were reproduced and used at the semiannual final review committee meeting. At this meeting all the official proposals at hand were considered and assigned an order of priority. To the extent that funds are available the procurement papers are later initiated. The investigations, with funds for two years, start about nine months after the initial inquiry. Ten or 12 months after the research is under way, it is our custom to request the budget for the second two years. Procurement action is then started, nine months in advance of expiration date, to extend the period of investigation for the final two years.

Generally we support an investigator four years. Further support requires another competitive proposal.

The case histories related emphasize the time and importance which we give to evaluation and selection of capable investigators with significant ideas on the frontier of new science in chemistry. Evaluators are a vital part of our competitive proposal selection process. They are distinguished research scientists whose combined interests cover most of chemistry and its border areas. Our relation with these men is unique because not one of them receives research funds from AFOSR.

The Scientific Payoff

So far a method of selecting significant new research areas has been discussed, but the mission of AFOSR, as previously mentioned, is also to *encourage* the maximum productivity of the selected investigators. This is done in the following ways:

1. By research awards through grants and contracts.
2. By generally granting support for four years at a time, so the researcher can concentrate on his research rather than the preparation of yearly requests.
3. By encouraging the researcher to direct his own work, to publish as he sees fit, and to require a minimum of useless reporting and other paper work.
4. By advising when necessary on the routes through governmental procedure on equipment, on travel, and concerning foreign assistance.
5. By moral support in visiting, in listening to accomplishments, and in listening to and showing appreciation for their research problems.
6. By suggesting other sources of funds to investigators with ideas outside our areas of research interest or beyond our means.
7. By sometimes explaining to the investigator why some proposals are not sufficiently competitive and thus fail to obtain support.

Summary data on AFOSR support may be of interest. Our budget in the fiscal year 1963 was about 3 million dollars; 2.7 million, fiscal year 1962. For a number of prior years it was approximately 2 million dollars.

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Accepting publications as an indication of merit and using papers appearing in 1960 and 1961 in three selected journals as a sample, our support is acknowledged in 129 papers or over 3⅓% of the total appearing in these three journals:

1960–61	Number	Per cent
J. Am. Chem. Soc.	54	2.37
J. Phys. Chem.	22	2.59
J. Chem. Phys.	53	4.24

The purpose of this paper is not to solicit additional proposals, but to describe one procedure for the selection of excellent investigators with significant research ideas. The author hopes it will be of assistance to those seeking research support.

In some circles it is stated and believed that all good research, all excellent investigators receive ample support. This is contrary to my experience. Although AFOSR ultimately adds 25 to 30 new investigators to its program each year, over three times that many, requesting 5 to 6 million dollars, now remain without our support. The fate of these can be estimated on the basis of earlier experience. In the six months ending August 1, 1961, from 144 informal proposals requesting 10 million dollars, 57 official proposals requesting 4 million dollars received final review and 33 of these requiring 1.8 million dollars were selected as excellent. Yet in September 1962, 18 months after many of the requests were prepared, about half of the 33 were still without funds from any source. This situation is a national tragedy, since these researchers are not yet creating that "new science" of tomorrow.

E. Fischer
The Weizmann Institute of Science
Rehovoth, Israel

Y. Hirshberg—In Memoriam

In the fast-moving world of today people, including scientists, tend to live in the future or, at best, in the present, and there is little room for sentiments regarding the past. It is therefore all the more appreciated by my friends at home and myself that Dr. Wyman and the organizers of this Symposium took the initiative to devote this session to Yehuda Hirshberg's memory, and also asked me to tell you a little about the man and his work.

Hirshberg's life was moulded to a large extent by his Jewish heritage and his Zionist background, both of which had a profound influence on his personality and career. After finishing high school in Poland, Hirshberg went to Palestine in 1923 as a pioneer and joined a collective settlement. This was in line with the Zionist ideals of that period, which put the accent on the transformation of the Jewish intellectuals into agricultural workers. However, after a year he fell ill with malaria, like so many of his comrades, and went to Jerusalem to recuperate. He started working as a manual laborer, but at the same time could not withstand the attraction of the Hebrew University and enrolled in it. The science division there was at that time still in its embryonic stage, but full of enthusiasm, with teachers and students forming a sort of family.

After five years of combined labor and studies he graduated, and soon won a scholarship to the University of Brussels. In the archives of our late President Weizmann we found the copy of a letter which he wrote to a friend in 1930. It read as follows:

> I understand that at the University of Brussels there is a Palestinian boy, a Mr. Yehuda Hirshberg, who is supposed to be a brilliant chemist. I have been told that in University circles he is known by the name of the "miracle of Jerusalem." He has done a considerable amount of good work at the University of Jerusalem; and I enclose copies of the course of studies he has taken. He is in straitened circumstances and would require a subsidy of about £4 per month, if he is to proceed with his scientific work.

Apparently Hirshberg got this financial help, because a year later he completed his post-graduate studies, won his doctorate with great distinction and attained an assistantship in the laboratory of Victor Heri, one of the founders of modern photochemistry and spectroscopy, and later worked with Errera, who was also an outstanding physical chemist. However, Hirshberg longed to return to Israel; and when asked by Weizmann to join the staff of the Sieff Institute in Rehovoth, which was just founded at that time, he gladly agreed and in 1933 returned to Israel. Thus began his life-long association with Weizmann and the Sieff Institute, which later developed into the present Weizmann Institute.

The 1930's and then the war years were a difficult period for the few Israeli scientists then existing. They had to struggle continuously with adverse external conditions, including of course the fact that they were a small isolated group, remote from the centers of research in Europe and America. Many of my own teachers belonged to this generation, which in a way was the "desert generation," who sacrificed their own

This paper introduced the session set aside to commemorate the late Professor Y. Hirshberg's contributions to the field of reversible photochemical processes at the April, 1962, International Symposium on Reversible Photochemical Processes in Durham, North Carolina, which was sponsored by The U. S. Army Research Office. Other original papers presented at this Symposium will appear in the *Journal of Physical Chemistry*.

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scientific careers in order to build the foundations of Israeli science today. Not all of them lived to have the satisfaction of seeing and harvesting the fruit of these hard years. Their effort has therefore to be appreciated all the more. However, Hirshberg lived to have this well-deserved satisfaction. Let me just outline his research until 1950. His first photochemical work dates back to 1933, when he studied, with Victor Henri, the photochemical decomposition of glycine. Later, already at the Sieff Institute, he investigated the photochemistry, in water solutions, of alcohols and aldehydes, and then the photochemical deamination of amino acids. This was followed by research on the photochemical interaction between primary and secondary alcohols and ketones, and then photochemical decomposition of solid hydrogen compounds at low temperatures. All this and related work is what is nowadays called "classical solution photochemistry." Concurrently he naturally got involved in absorption spectroscopy and in this field gradually moved through the various experimental stages, starting with the slow and laborious spectrophotographic methods of the early years, then passing the "Beckman DU" stage, and ending with the Cary Recording Spectrophotometer. At the same time he investigated fluorescence spectra and tried, like others, to find some correlation between the spectra and the structure of large organic molecules, as well as their carcinogenic activity. A sojourn in Ottawa at Norman Jones' laboratory resulted in papers on the UV spectra of carboxylated naphthalenes. His first publications on photo-isomerization, involving arylated butadiene, appeared in 1950.

At this period he became interested, through Ernst Bergmann, in thermochromic dianthrones, and late in 1950 made his discovery of the phenomenon named by him "photochromism," namely the reversible transformation of these colorless compounds into colored forms by the action of ultraviolet light. Since then the term "photochromism" has become quite popular among workers in this field and, although it is not too well-defined, I am glad that Hirshberg is also commemorated in this way.

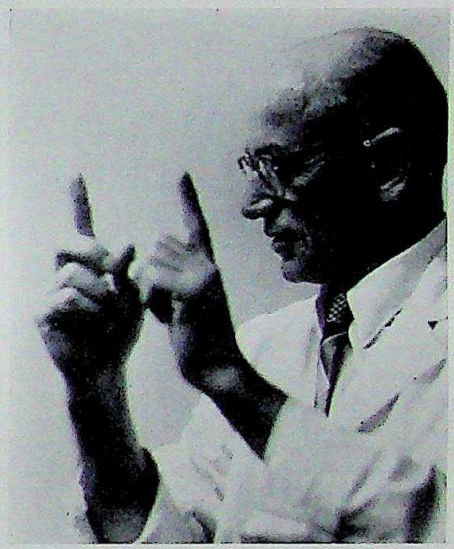
This first discovery was soon followed by a similar one with spiropyrans, and then by the reverse reaction with visible light. These exciting topics of research gave Hirshberg an ample opportunity to use his knowledge and capabilities to the fullest extent. His zeal and enthusiasm were boundless, and I should mention in particular his stubborn belief that these systems might eventually be used as information storage and handling devices, as well as image-forming media. This was in spite of the declared skepticism and criticism of many of his colleagues, who did not appreciate sufficiently the man and his work. The results of those fruitful years are well-known.

To describe Hirshberg during this period, let me quote a colleague who, unfortunately, said these words only as an obituary:

Dr. Hirshberg belonged to the ever-decreasing group of scientists who consider their day well spent at the bench, away from the many distractions which life presents today. His pride in being active in the laboratory was an inspiration to his hard-working group and surely to all of us. I well remember his phenomenal skill as an experimenter, and often admired his quick and nimble hands, and above all his ability to perceive results. In an age where instrumentation, automatic recording and all such gadgets have become the be-all and end-all of experimental work, his observational skill was a pleasure and an example to behold.

It was his skill and his patience at the bench that led to his observations of the complex photo-behavior of organic compounds on which he and his group have been working. It is rare today that a man can show a record of research around a central theme; Yehuda Hirshberg worked on the interaction of radiation with organic molecules over 26 years of scientific activity, and throughout those years he constantly succeeded to maintain a fresh approach to his central problem.

We shall never know now how far his own work would have progressed; but no better tribute can be paid to Yehuda Hirshberg's research than this: since the publication of his major papers interest in the phenomenon of photochromy has exploded worldwide.



Despite his success, Hirshberg never ceased to be a "man of the people," being on friendly terms with everybody, irrespective of grade or standing. His personality was marked by boundless devotion to his work, willingness to help, and eagerness to make a friend of whomever he met, a goal which he achieved almost always thanks to his rich Jewish humor and his good-heartedness.

His last years were marred by great suffering because of his many maladies. Nevertheless, he put up a stubborn fight against his disease and refused to give in. He was active in the laboratory and full of plans to his last day, and succumbed to a heart attack while still wearing his white laboratory coat. It is sad indeed that he thus did not live to see the widespread applications of photochromism, which are apparently ahead of us today.

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Division of CHEMICAL EDUCATION
American Chemical Society

. . . report from the EXAMINATIONS COMMITTEE

T. A. ASHFORD, Chairman

The Examinations Committee, in its 33rd year, is constructing and distributing standardized tests in all fields of chemistry. The early tests were prepared for the first year of college chemistry, but gradually the scope has been extended and now includes two or more forms in Qualitative Analysis, Quantitative Analysis, Organic Chemistry, Physical Chemistry, Biochemistry, and Inorganic Chemistry. Recently a battery of tests in Analytical, Organic, and Physical has been prepared for the use of graduate schools to test entering graduate students. In cooperation with NSTA, a joint subcommittee released the first high school test in the field in the spring of 1957, followed by six additional forms, including Form 1963 and Form 1963ADV. Form 1963ADV has been constructed to meet the demand for a higher level, more difficult high school test. A total of 27 tests is sponsored by the Committee—17 college level, seven high school level, and three graduate level. In addition, nine "retired" college tests have been released to high school teachers for use in advanced "college level" courses. Extensive norms have been prepared for all tests based upon reports of previous testing programs.

During the past years there has been an increase in all aspects of the Committee's work, including sales, so that the Committee is in better financial condition than ever before. An estimated 300,000 college and high school students were tested this past year, based upon the sales of tests and answer sheets to 895 colleges, 1015 high schools, and 89 graduate schools. Only the high schools sales showed a slight decrease. Three tests were made available in the spring of 1962: Organic Chemistry Form 1962 for the year course, under the direction of Dr. Nelson; General Chemistry Form 1960S, under the direction of Dr. Dexter; and High School Chemistry Form 1961S, under the direction of Mr. Headlee. In addition, the Graduate Level Tests, whose use had previously been restricted, were released to all schools offering a PhD program in chemistry or chemical engineering. New tests are in preparation for all fields from high school through graduate level. The 1963 Testing Program, with the three new tests released this March, is described below

The Committee's work has taken on an international flavor since several of the tests have been translated into other languages. The High School Forms 1959S and N have been translated into Japanese, the General Form 1958 into Indonesian, the General Form G into Portuguese, and the General Form G and High School Form 1959 into Spanish. Inquiries from high schools and universities have been received from many countries, especially Western Europe and Latin America. One request from Japan invited a Committee representative to instruct them in the construction of tests.

The Committee expresses its appreciation to the University of South Florida for their services, since the University's overhead subsidy provides—without charge to the Committee—the space to carry out the secretarial and shipping work, as well as the use of IBM equipment. Also, the Committee is grateful for the help of schools and colleges represented by the members of the subcommittees.

The goal of the Committee's work is to improve the teaching of chemistry through its testing program. The Committee invites all chemists to participate in this program by associating with the subcommittee of major interest. The interchange of ideas brings the important concepts into focus for both teaching and testing.

For the Committee:
BERNARD A. NELSON
WHEATON COLLEGE
WHEATON, ILLINOIS

1963 Testing Program

Three new tests have been published for 1963:

General Chemistry, Form 1963. A 105 minute test, in three parts, to measure achievement in general college chemistry including recall of information, application of principles, methods, techniques, problems and calculations. Constructed by the General Chemistry Subcommittee under the chairmanship of Dr. Forrest P. Dexter.

High School Chemistry, Form 1963. The latest in the regular series of high school chemistry tests (90 items, in two parts requiring 40 minutes each) constructed by High School Chemistry Subcommittee I, under the chairmanship of Mr. Elmer Headlee. The subcommittee was appointed jointly by the National Science Teachers Association and the Examinations Committee—ACS.

High School Chemistry, Form 1963ADV. An experimental test (70 items, in two parts requiring 40 minutes each) constructed specifically for advanced or superior high school chemistry courses by High School Chemistry Subcommittee II, under the chairmanship of Mr. Kermit Waln. The subcommittee was appointed jointly by the National Science Teachers Association and the Examinations Committee—ACS.

In addition to the ones above, the following tests are available:

General Chemistry, Forms 1960, 1960S, 1958, and 1958S
Qualitative Analysis, Forms 1960 and H
Brief Qualitative Analysis, Form 1961
Qualitative Analysis Supplement for General Chemistry, Form J
Quantitative Analysis, Forms N and G
Organic Chemistry, Forms 1962 and 1958
Brief Organic Chemistry, Form 1961B
Physical Chemistry, Form L
Inorganic Chemistry, Form 1961
Biochemistry, Form 1959
High School Chemistry, Forms 1961, 1961S, 1959, 1959S, and N
Graduate Level Placement Examinations in
Analytical Chemistry
Organic Chemistry
Physical Chemistry

These tests are confidential and are available only to members of educational institutions. For further information and a brochure describing the tests write to the Examinations Committee—ACS, University of South Florida, Tampa, Florida.

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Condensed Norms: ACS Cooperative Examinations

Three new tests were released in the spring of 1962: Organic Chemistry Form 1962, General Chemistry Form 1960S (a scrambled version of Form 1960), and High School Chemistry Form 1961S (a scrambled version of Form 1961).

In addition, the Graduate Level Subcommittee, under the chairmanship of Dr. Harry G. Day, released three Graduate Level Placement Tests in 1962: Analytical Chemistry Form 1961A, Organic Chemistry Form 1961O, and Physical Chemistry Form 1961P. These tests are now available to schools offering a PhD program in chemistry or chemical engineering.

The condensed norms are selected from a much larger body of data which can be obtained from the Examinations Committee, American Chemical Society, Theo. A. Ashford, Chairman, University of South Florida, Tampa, Florida.

Graduate Placement Test in Organic Chemistry

Form 1961O was prepared by a subgroup consisting of:

J. F. Bunnett, Brown, Chairman
F. M. Beringer, Polytechnic Institute of Brooklyn
R. E. Silker, Kansas State
C. A. Vander Werf, Kansas

Seventy items are presented, each requiring the choice of a correct answer from among five alternatives. Ninety minutes are alloted. Items are not ordered according to topics; this tends to emphasize the comprehensiveness of the examination. Essential information is tested (topics such as nomenclature, laboratory practice, synthesis, and identifications). Modern views of mechanistic interpretation, electronic structure, optical isomerism, and conformational analysis are expected.

Condensed Norms

Scoring formula Maximum possible score	R-W/4 70
Percentile rank	
99	63.6
95	56.8
90	51.4
85	48.0
80	44.0
75	41.1
70	38.8
65	36.4
60	34.2
55	31.1
50	29.1
45	27.3
40	25.4
35	23.7
30	21.1
25	18.6
20	15.6
15	12.4
10	9.5
5	5.9
1	1.5
Reliability coefficient	0.954

The figures given are raw scores.
The reliability coefficient was estimated by the Kuder-Richardson Formula No. 21.

The group consisted of 489 first year graduate students in 25 institutions.

Graduate Placement Test in Analytical Chemistry

Form 1961A was prepared by a subgroup consisting of

R. C. Bowers, Northwestern, Chairman
G. H. Ayres, Texas
W. W. Brandt, Kansas State
H. B. Williams, Lousiana State

Thirty multiple-choice questions require 90 min. The test is designed to indicate a balanced coverage of modern analytical chemistry. About 40% of the questions would not have been on such a test five years ago. A student needs to know more than classical stoichiometry; he needs to have had experience with electroanalytical, spectral, and other instrumental techniques as well as to know something about chelometry and separation methods.

Condensed Norms

Scoring formula Maximum possible score	R-W/4 30
Percentile Rank	
99	22.4
95	18.3
90	16.6
85	14.9
80	13.8
75	12.8
70	12.0
65	11.0
60	10.1
55	9.5
50	8.6
45	7.8
40	6.8
35	6.0
30	5.2
25	4.3
20	3.2
15	2.3
10	1.1
5	0.2
1	0.0
Reliability coefficient	0.877

The figures given are raw scores.
The reliability coefficient was estimated by the Kuder-Richardson Formula No. 21.

The group consisted of 342 first year graduate students in 18 institutions.

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Graduate Placement Test in Physical Chemistry

Form 1961P was prepared by a subgroup consisting of

J. D. McCullough, UCLA, Chairman
R. A. Alberty, Wisconsin
C. N. Caughlan, Montana State
J. J. Jasper, Wayne State
J. A. Ricketts, DePauw

Twenty items are included; all are of the multiple-choice answer type. Ninety minutes is the prescribed time. Fundamental thermodynamic principles loom large; equilibrium, kinetics, electrochemistry, and other major areas are represented. A student also must have a thorough understanding of how information at the molecular level can be used to anticipate macroscopic properties.

Condensed Norms

Scoring formula Maximum possible score	R-W/3 20
Percentile rank	
99	16.2
95	12.9
90	10.9
85	9.3
80	8.4
75	7.4
70	6.5
65	5.7
60	5.1
55	4.5
50	4.1
45	3.6
40	3.1
35	2.5
30	1.8
25	1.2
20	0.7
15	0.3
10	0.1
5	0.0
1	0.0

The figures given are raw scores.

The group consisted of 522 first year graduate students from 22 institutions.

Organic Chemistry Form 1962

Form 1962 follows the same format as the 1958 form. Five possible responses are given for each question. Part one (50 items, 50 min) deals with monofunctional aliphatic compounds. Part two (50 items, 50 min) covers aromatic compounds, polyfunctional compounds, and natural products. At least 15% of the 100 items deal with material which has only lately entered the introductory organic chemistry course. The new form gives greater emphasis to such content as correlations of physical properties to structure and reaction mechanisms. Two or three items reflect very recent entries into the descriptive portion of the course.

Condensed Norms

Scoring formula Maximum possible score	R-W/4 100
Percentile rank	
99	86.3
95	71.9
90	65.8
85	61.6
80	58.4
75	54.6
70	51.1
65	48.7
60	46.3
55	43.5
50	41.3
45	39.5
40	37.6
35	34.5
30	32.1
25	29.7
20	26.8
15	23.0
10	19.4
5	15.1
1	8.7
Reliability coefficient	0.940

The figures given are raw scores.

The reliability coefficient was estimated by the Kuder-Richardson Formula No. 21.

The group consists of 763 students who took the test at the completion of a one year course in organic chemistry. The semester hours ranged from 8–11, with a mean of 8.5. Lecture hours ranged from 2–4 per week, with a mean of 3.0. Laboratory hours ranged from 3–6 per week, with a mean of 4.2.

Addendum: Conventions Defining Thermodynamics

Professor Albert Sprague Coolidge of Harvard has called my attention to an ambiguity in my paper on "Conventions Defining Thermodynamic Properties of Aqueous Ions and other Chemical Species" (THIS JOURNAL, 40, 2 (1963)).

The entries for gaseous ions in Table 2 were based on entries in Bureau of Standards Circular No. 500. Although the conventions are not clearly stated in that Circular, the entry for $\Delta H_f°$ for gaseous sodium ion is really $\Delta H°$ for the reaction

$$Na(c) \rightarrow Na^+(g) + e^-(g)$$

Hence it includes $(5/2)RT$ for the translational energy and PV work associated with creating the gaseous electron even though the electron is not mentioned in the entry.

Similarly, the entry in Circular No. 500 for $\Delta H_f°$ for gaseous chloride ion is really $\Delta H°$ for the reaction

$$^1/_2Cl_2(g) + e^-(g) \rightarrow Cl^-(g)$$

Hence the sum of the enthalpies of the species on the left side of the equation is assumed to be $(5/2)RT$ rather than zero.

Because the Bureau of Standards conventions differ from what I thought they were, and since it is essential that contributions from gaseous electrons be separated if reactions of Type G are to be discussed, the entries in Table 2 of my paper must be changed. For every positive gaseous ion of charge $+z$, values of $\Delta H_f°$ and of $\Delta F_f°$ in Table 2 should be made less positive by $1.481z$ kcal/mole; for every negative gaseous ion of charge $-z$, the values should be made less negative by the same amount. If these changes are made, the entries in Table 2 will be consistent with the text of the paper.

If these changes are made, values of $\Delta H_H°$ and of $\Delta F_H°$ in equations (35) and (36) of my paper must also be reduced 1.48 kcal/mole. As will be pointed out in a forthcoming paper in the Journal of the American Chemical Society, these thermodynamic changes for reaction (34) assume that the electron in state $e^-(0)$ is in a medium at the bulk electrostatic potential of water rather than in vacuum. The distinction is only important when "absolute" electrode potentials are being considered.

RICHARD M. NOYES

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The Physical and Chemical Character of Graphite

Carbon exists in two main crystalline forms, diamond and graphite. Many other forms of "amorphous carbon" exist which are actually microcrystalline in character but are of a less orientated nature. Diamond, charcoal and lamp-black were well known to the ancients, but considerable confusion arose in the history of graphite because of its mineral similarity to molybdenum disulfide.

The true history began when Scheele (*1*) showed the individual nature of graphite and four years later Lavoisier demonstrated that graphite and diamond are allotropic forms of carbon. The interconversion of these allotropes has been discussed in detail by Hall (*2*). Perhaps the greatest spur to the study of graphite was given by the pioneering work of Acheson in producing graphite on a commercial scale resulting for example in the eventual wide use of colloidal graphite as a lubricant (*3*). Today a large industry is built upon the results of Acheson's master patent and in this review we would wish to touch on some aspects of the properties of this versatile material.

Occurrence and Manufacture

Natural Graphite. Graphite occurs naturally; it is so widely distributed over the earth's crust that it is mined in such widely separated places as Ceylon, Madagascar, the United States of America, Canada, Korea, and Bavaria. It is generally found associated with substantial quantities of mineral impurities, the bulk of which is removed usually by hand but in some cases a washing process is employed; further treatment, however, is required before a relatively pure material is obtained. It has been found that repeated washing of the graphite, successively, with concentrated hydrochloric and hydrofluoric acids reduces the ash content to a small value. Other methods of purification have been reported such as, for example, treatment of the natural graphite with carbon tetrafluoride and sulphur hexafluoride and heating with sodium carbonate and chlorine. When the latter method is used, heating *in vacuo* to temperatures in the region of 2500 to 3000°C is recommended to remove any retained halogen in order that graphite of the highest purity may be obtained.

Natural graphite generally has a metallic luster when freed of mineral matter; translucent and even transparent crystals are said to have been found. Single crystals which also occur in the deposits of natural graphite have been used, after purification, in a number of fundamental studies on graphite (*4*) and (*5*). Attempts to produce single crystals of graphite in a high state of purity have been reported by Foster, Long and Stump (*6*), who decomposed single crystals of aluminum carbide (Al_3C_3) by heating to a temperature of about 2500°C. The aluminum volatilized leaving a residue which was shown to possess the appropriate graphite crystal structure.

Kish Graphite. A crystalline but rather impure material known as Kish graphite separates during the cooling of molten cast iron when excess carbon crystallizes from the melt. Further purification using the techniques described above yields a product similar in appearance to natural graphite.

Artificial Graphite: Acheson Process. The manufacture of artificial graphite can be said to have had its beginnings during the latter part of the last century when Acheson in the USA observed a crystalline deposit on the cooler parts of the electric furnace in which he was trying to produce silicon carbide (carborundum) by heating a mixture of coke and sand to a high temperature; the deposit was in fact graphite. Acheson then proceeded to exploit his discovery that on heating an amorphous carbon to a high temperature crystallization occurs and graphite is formed. After carrying out a great many experiments using carbons from a number of different sources he eventually concluded that anthracite was the material most easily converted into graphite. In this early work, Acheson's electric furnace consisted of a firebrick box through the center of which a carbon rod was passed horizontally, the material to be heated being packed round the central electrode; connection of the electrode to a suitable supply of electric current then enabled the furnace to be raised to the required temperature.

Modern Method of Manufacture. The manufacture of artificial graphite today is still based on the original Acheson process, the main difference being that granules of carbon powder are bonded together to form an artifact before heating to the high temperature required for graphitization.

Carbon from a number of sources is being used at the present time, for example, lampblack, anthracite, pitch coke, and coke made from the residue of petroleum distillation; but not all carbons are suitable for conversion to graphite (*7*). The carbon is first calcined at a temperature of about 1000°C in order to remove volatile matter and then ground to a coarse powder. The coke powder with a carefully controlled particle size is mixed with binder, usually tar or pitch, in the proportions of about three parts of coke to one part of pitch, to give a plastic mix which can then be pressed or extruded into any desired shape.

The "green" shape is fired or baked by slowly raising the temperature to about 1000°C when partial volatilization and carbonization of the binder occurs. At this stage in the manufacture impregnation of the

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artifacts with pitch or other suitable materials—for example, furfuryl alcohol or sugar—is carried out if products of higher density and lower permeability to gases are required; a further period of baking after impregnation is then necessary.

Conversion of the extremely hard artifact into the softer graphite—the process of graphitization—is achieved by slowly heating the material to a temperature of between 2700 and 3000°C in an electric furnace. The baked shapes are stacked in the furnace and packed with powdered petroleum coke to give good electrical continuity throughout and to ensure that graphitization proceeds in a non-oxidizing atmosphere.

During graphitization crystal development takes place with the formation of the typical layer structure of graphite. This high temperature treatment improves the purity of the product since volatilization of contaminants also takes place. Further purification, especially where applications in the nuclear energy field are envisaged, is achieved by heating to 2500°C in a stream of chlorine or fluorine gas (*8*). As a result of the manufacturing process, the product, though polycrystalline, has imparted to it anisotropic behavior because of some preferred orientation present in the original coke particles. It is found in the extruded shapes that the particles tend to align themselves with their long axes parallel to the direction of extrusion while in the pressed or molded shapes the long axes are perpendicular to the direction of the applied force.

Pyrolytic Graphite

More recently, the demand for graphitic materials that are resistant to oxidizing atmospheres and less permeable to gases has resulted in a considerable amount of research being carried out with this end in view. Processes are now available to produce a dense carbon possessing these properties, this material being known as pyrographite. The method is based on the thermal decomposition (pyrolysis) of simple hydrocarbon molecules, for example, methane, ethane and benzene, at temperatures in the region of 2000°C at reduced pressures (*9*) and (*10*). The product is a deposit consisting of graphite crystallites highly aligned with the dimensions of the substrate surface. The deposits are extremely dense with a value approaching the theoretical figure for the crystalline graphite. Pyrographite can be made as thin protective coatings on conventional graphite or on other substrates as well as free standing shapes, though the latter are, for the present, confined to small articles.

Physical Properties

Crystal Structure. The crystal structure of graphite was first deduced by Bernal (*11*) from X-ray diffraction photographs. Other workers have since confirmed the structure proposed by Bernal which is depicted in Figure 1. Essentially graphite consists of layers of hexagonal arrays of closely packed carbon atoms, the layers being stacked in such a way that alternate ones lie immediately above or below one another thus giving a stacking sequence of *ab ab*, etc. However, a number of lines in the X-ray diffraction patterns have been identified with a sequence in the layer stacking of *abc abc*, etc., but this form has been found to occur to the extent of only about 10 to 15% in many graphites. This more complex lattice is metastable and can be converted to the *ab* form by heat treatment.

The positions of the carbon atoms in the layer planes are determined by the sp^2 hybridization typical of an extended aromatic structure. The carbon-carbon bond length of 1.42 Å is close to that of 1.39 Å found in appropriate positions in the benzene ring (compare the sp^3-σ-bond length of 1.54 Å in diamond or saturated hydrocarbons). Considerable overlap occurs between the π-orbitals of this macromolecular array, resulting in a mobile electronic system characteristic of the semi-metallic state. In contrast, however, to this tight bonding within the layer planes only weak van der Waals forces are responsible for the cohesion between adjacent planes as indicated by the value for the interlayer spacing of 3.35 Å.

As might be expected from these crystallographic considerations, graphite exhibits anisotropy which is manifested in many of its physical properties such as thermal expansion, thermal and electrical conductivity and hardness. Thus, it is found that the value obtained for a particular physical property is dependent upon whether the measurement is made in the direction of the layer planes or perpendicular to them. By calculation using the lattice parameters the theoretical crystal density of graphite is shown to have a value of 2.265 g/ml. Because of various defects a given piece of graphite, natural or artificial, is rarely found to possess the ideal structure throughout. The density of natural graphite often approaches a value of about 2.2 g/ml but that of artificial material is very much lower.

Pore Structure. The method of manufacture of artificial graphite gives a product having a lump density of 1.6 to 1.8 g/ml, a value which is much less than the theoretical density. This difference in density indicates the presence of voids within the graphite artifact amounting to about 30% of the total volume (*12*). Since artificial graphite is an agglomerate of graphitized coke particles bonded together with a graphitized binder, both of which are produced by the decomposition of hydrocarbons, it is not difficult to visualize that the resulting solid product possesses a complex network of interconnected capillaries and cavities (Fig. 2). During graphitization crystal growth occurs with alignment of the layer planes but the final size of the crystallites is limited by the grain boundaries of the original coke particles so that most of the interparticulate porosity remains. A contribution to the porosity will also come from the voids inherent in the coke granules themselves. In addition to the accessible porosity it is often found that there is a small proportion of pores present that remain inaccessible even to the small atoms of helium amounting to about 4% of the total porosity for a typical reactor graphite. It is possible that oxidation will cause these pores to be made accessible (*13*).

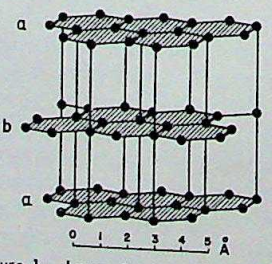


Figure 1. Layer structure of graphite.

Associated with this internal volume is an internal surface area that is many times that of the external or geometrical surface; thus the extensive capillary structure present in

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artificial graphite produced in this way may impose serious limitations on its use where reactive gases or liquids are likely to come into contact with the graphite. Considerable control is likely to be exercised by the capillaries over the rate at which the reactants can enter, and the products leave, the system of pores. The theoretical treatment of porous catalysts elaborated by Thiele (*14*) and Wheeler (*15*) has recently been applied to gas-carbon reactions (*16*).

It is evident from the foregoing remarks that graphite is likely to show considerable variation in its properties and consequently the value obtained for any property relates only to the particular sample being examined, and the figures quoted must be regarded as representing the range of values rather than the absolute ones for a given characteristic.



Figure 2. Photomicrograph showing the porous nature of artificial graphite.

Graphite is a good conductor of both heat and electricity thus resembling many of the metallic elements. The following are typical values for the thermal conductivity and the electrical resistivity of an artificial graphite, at room temperature, illustrating the anisotropic character of the material.

	Parallel to Layer Plane	Perpendicular to Layer Plane
Thermal Conductivity (cal/cm-sec °C)	0.3–0.5	0.2–0.3
Electrical Resistivity (milliohm-cm)	0.5–0.8	0.8–1.2

Figures 3 and 4 show the variation of these properties with temperature.

The thermal expansion of graphite is also markedly anisotropic; for example, in the temperature range 0 to 150°C the coefficient of thermal expansion perpendicular to the layer planes has a value of 286×10^{-7} cm/cm°C and is positive, while that along the layer planes is negative and has a value of -15×10^{-7} cm/cm°C over the same temperature range.

Because of its low vapor pressure (approximately 5×10^{-6} atmosphere at 2500°C) graphite is valuable as a high temperature constructional material; it also has good mechanical strength under such conditions. It begins to sublime in the region of 3500 to 4000°C, the triple point being at approximately 100 atmospheres. The heat of sublimation of graphite, to which a value of 170 kcal-mole^{-1} has been assigned, is of considerable theoretical significance in calculating bond energies. Since it has not been measured directly by calorimetric methods, some controversy has arisen over this value estimated from spectroscopic and other thermal data. The conflicting evidence has been discussed by Kern (*17*). The heat of combustion of graphite is 94 kcal-mole^{-1}. The mechanical properties again exhibit the strong anisotropic behavior typical of the layer structure of graphite. The most remarkable fact about the strength of graphite is that it increases with temperature, reaching a value at about 2500°C which is nearly double that at room temperature, thus making it one of the strongest materials available where strength at high temperature is required.

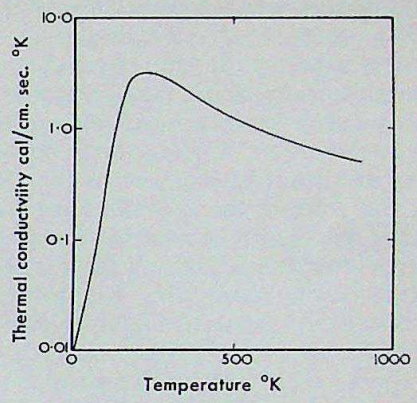


Figure 3. Variation of thermal conductivity with temperature.

Chemical Properties

The structural π-σ anisotropy of graphite affords a convenient classification of the reactions of graphite. Firstly, there are those reactions where the molecular weight of the graphite macromolecule increases by intercalation and bonding with the π-electron system involving, of necessity, the swelling of the macromolecule in a direction perpendicular to the basal plane. Secondly, there are reactions involving rupture of σ-bonds with concurrent breakdown of the lattice into smaller fragments. Energetically the first sequence, where bonding occurs with the mobile electron cloud within the structure, should be a relatively easy maneuver compared to the second case, where the separation of carbon atoms is attended by a high activation energy. It is convenient to classify further the intercalation compounds as homopolar (or covalent adducts) and heteropolar (or ionic compounds) both processes occurring via a number of steps or "stages." The homopolar products might be expected to result from an

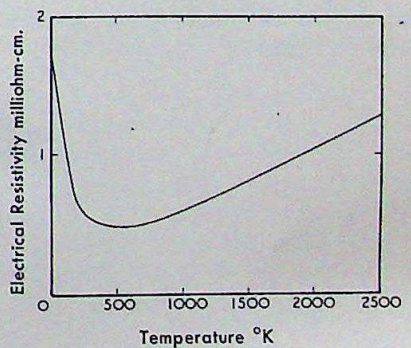


Figure 4. Variation of electrical resistivity with temperature.

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exothermic reaction with the more electronegative elements (*vide* CF_2 and CO_2).

The earliest compound of graphite to be studied (*18*) was graphite oxide (graphitic acid) prepared by oxidizing graphite with concentrated nitric and sulphuric acids containing some potassium chlorate. The solid product is unstable and photosensitive (*19*), decomposing exothermically to carbon monoxide, carbon dioxide, and water, together with some amorphous carbon. The interlayer spacing of the graphite lattice can be shown by X-ray examination to have swollen to more than 6 Å and the structure can further imbibe water to swell to more than 12 Å. The exact nature of the carbon-oxygen linkages is not well defined, in spite of a century of experimentation, recently involving modern chemical and physical techniques. It appears most likely that oxide bridges have been established across alternative carbons in the layer structure and a number of oxo groups introduced at primary carbon sites. In this process the planar sp^2-hybridized character of the graphite layer lattice has reverted to a puckered sheet of six-membered (sp^3-hybridized) carbon rings in the all-chair conformation (*20*). This structure has been further refined by Hofmann (*19*) who proposes a keto-enol tautomeric effect within the structure. This form (Fig. 5) fits in well with the accepted empirical formula $C_8O_2(OH)_2$, for the macromolecule. In less well ordered graphites, hydroxylic, ketonic, ketenic, lactonic, and carboxylic groups can be identified (*21*).

A further oxide of carbon has recently been discovered (*23*) where carbon atoms in the layer lattice are substituted by oxygen atoms. The "red carbon," $(C_3O_2)_n$ is obtained by the polymerization of carbon suboxide, and shows X-ray diffraction patterns characteristic of a monocrystalline carbon. Prolonged oxidation of graphite can also result in the formation of mellitic acid $C_6(OH)_6$.

The reaction of graphite with fluorine is very rapid and only gives a clearly defined stable monofluoride, C_nF_n, under carefully controlled conditions (*22*). The structure proposed by W. Rüdorf and G. Rüdorf consists of a macro sp^3-hybridized carbon sheet, in the all-chair conformation, with all axial positions occupied by fluorine atoms. The infra-red absorption spectrum of carbon monofluoride is very similar to that of a perfluoropolycyclic organic molecule. Compounds with a still higher carbon-fluorine ratio possess the planar aromatic graphite lattice structure with the correspondingly higher electrical conductivity; they also are darker in color than samples of carbon monofluoride.

Perhaps more important industrially are the graphite compounds containing ionic linkages. Donation or acceptance of electrons by the graphite layers produce changes in the "hole carriers" in conduction bands; whereas with the wholly covalent compounds the σ-electrons are completely localized. Where graphite can act as an anion, electronic interaction between the cation of the reactant and graphite must be possible, and also the electron affinity of the cation for the π-electrons must be adequate. Intercalation does not depend on the electronic configuration of the anion associated with the intercalated cation.

The lower members of the alkali metal group (potassium, rubidium and caesium) react readily with graphite. The adducts are formed by forcing the equilibrium

$$\text{Graphite} + \text{metal} \rightleftharpoons \text{adduct}$$

to the right hand side, by increasing the concentration of metal in the liquid or vapor form. The ratio of metal to graphite increases in stages; with increasing metal concentration the uptake of metal occurs first on the areas of higher graphitic character, e.g.,

$$\underset{\text{Dark grey}}{C_{60}K} \rightarrow \underset{\text{Blue}}{C_{48}K} \rightarrow C_{36}K \rightarrow C_{24}K \rightarrow \underset{\text{Bronze}}{C_8K}$$

The alkali metal adducts are extremely reactive, often igniting spontaneously in air and reacting violently with water or alcohols to produce the alkali hydroxide and hydrogen. Many different structural arrangements have been proposed for these compounds, but the simplest version is that due to W. Rüdorf and E. Schulze (*24*), for the compound C_8K. The graphite layer planes are assumed to be arranged so that carbon atoms are vertically above and below similarly environed atoms in adjacent sheets. The potassium atoms are situated between the sheets arranged equidistant from twelve surrounding carbons and are themselves equally spaced due to mutual repulsion forces. The compounds with higher carbon-metal ratios are sandwiches of varying sequential complexity and unappetizing filling (*25*). Sodium and lithium are reluctant to enter the graphite lattice and ternary lammelar compounds are only formed when traces of impurities are present. The impurities are thought to preferentially occupy "spacer positions" in the lattice, thus facilitating entry of lithium or sodium (*26*). When formed the lithium and sodium intercalates appear to be more stable than their potassium counterparts. Further expansion of the graphite lattice occurs when the alkali metals are absorbed in the presence of ionising solvents such as liquid ammonia or aliphatic amines. Measurements of paramagnetic susceptibilities indicate that these amine-metal-graphite complexes are similar in structure to their metal-graphite analogues. The polar character of the metal-graphite compounds is readily shown by the increase in electrical conductivity of the macromolecule after intercalation, indicating an increase in the number of electrons held in the conduction band of the graphite anion.

During the aqueous oxidation of graphite a further complication occurs since the more stable anions present in solution may be reversibly introduced into the lattice. (The primary oxidation step removes π-electrons from the graphite leaving a positively charged interlayer space.) A typical graphite salt, where graphite acts as a cation, is a graphite bisulfate $C_{24}^{+}\ HSO_4^{-}\cdot\cdot 2H_2SO_4$, formed by oxidation of graphite with concen-

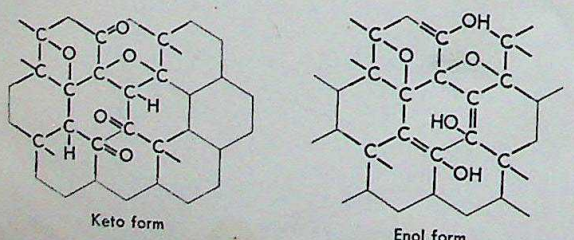


Figure 5. Graphite oxide layer (after Hofmann (*19*)).

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trated nitric and sulfuric acids. This product is only formed from Kish graphite or natural material, and not from less ordered material. The "graphiteonium salts" are instantly decomposed by water and many organic materials; in the presence of other anions, for example, trifluoroacetate ion, they will undergo a process of anion exchange to give a more stable salt. The structures of these salts are analogous to those of the metal-graphite complexes, but in these instances the graphite acts as a *p*-type conductor whose predominant carriers become positive holes.

Polar graphite-halogen compounds are known, but it is likely that in the case of the bromine compounds, for example, a large proportion of the bromine may be intercalated as unionized molecules. Graphite chloride is even less well characterized although the existence of C_8Cl, at temperatures below 0°C, has now been established (*27*). A wide range of metal chlorides, oxides and sulfides (usually of the transitional metals in their higher valency states) can be intercalated in graphite. These complexes are of varying composition and stability, the salts being slowly leached out of the lattice by aqueous solvents.

The process of intercalation is troublesome when graphite is used as a container material for these compounds or elements, the graphite structure slowly breaking down and decreasing in mechanical strength. Intercalation can be prevented by cross-linking the graphite planes, or by cleaning up the lattice defects, as in the stabilization of man-made or natural polymers. An excellent discussion of the thermodynamic implications of intercalation phenomena is given by A. R. Ubbelohde and F. A. Lewis, and general reviews on intercalation by Croft and Hennig (*28*).

The chemical reactions of graphite thus range from the equimolar stoichiometric reactions, where the final product may have a carbon conformation different from that of the starting material, to the reactions associated only with surface defects and lattice vacancies. In the technological applications of graphite the latter type of reaction is the more important one, as small defects in the lattice would undermine the mechanical features of graphite in relation to its use either as a structural material or as a lubricant.

The transformation of graphite to volatile products involves principally the reactions with oxygen, carbon dioxide, hydrogen, or water (*29*). Standard experimental methods used for following the progress of such reactions involve the measurement of volume or weight changes, or in favorable circumstances radioactive tracers may be employed (*30*). The temperature of the graphite surface is varied by the conventional furnace or eddy current heating techniques, but a novel method involves heating the graphite by employing the graphite specimen itself as the resistance heater element. In all this work involving reaction of a gas with a solid graphite surface the questions of purity, temperature, pressure, gas-solid contact time, particle size, surface area, porosity, and pre-treatment, such as handling, of the graphite surface must be taken into account and an assessment made of their possible influence on reaction rate. More recent work on the gas-graphite reactions has emphasized the importance of the effect of lattice defects on the reactivity of graphite (*31*), in contrast to the older assumptions that reaction only occurred at corner and edge atoms of the lattice. The high reactivity of dislocations and defects in freshly cleaned natural graphite has been strikingly shown by E. E. G. Hughes and J. M. Thomas (*5*). A study of the topography of graphite crystals heated in oxygen shows that gasification of carbon commences at surface atoms in the basal plane and proceeds in a direction perpendicular to it, that is, along the C-axis of the molecule. This process results in well defined hexagonal oxidation pits only at the sites of lattice vacancies or dislocations. The pitting is enhanced by traces of metals, or chemisorbed hydrogen or oxygen irreversibly bonded at these sites. In marked contrast, the topography of graphite remains unchanged when treated with carbon dioxide, even for long periods at 900°C.

Kinetic investigation of the reaction between oxygen and graphite has shown a first stage where the formation of a "surface oxide" occurs at an "active site" on the surface:

$$2C + O_2 \rightarrow 2C(O)$$

The nature of the surface oxide is still controversial and it may sometimes be strongly chemisorbed carbon monoxide. The second reaction stage involves the gasification of carbon as carbon monoxide:

$$C(O) \rightarrow CO$$

It appears likely that carbon monoxide is the first major reaction product in reactions with highly ordered graphites and that subsequently carbon dioxide is formed either by a homogeneous or heterogeneous oxidation (*32*). Other intermediates such as carbon suboxide have been observed in the oxidation of imperfect or radiation damaged graphites.

Reaction of graphite with carbon dioxide also proceeds via a surface oxide mechanism:

$$C + CO_2 \rightleftharpoons C(O) + CO \rightleftharpoons 2\ CO$$

The first equilibrium stage is the predominant reaction at temperatures below 500°C, and no loss of carbon from the graphite surface is observed (*33*). In a closed system the equilibrium is well to the left in the above equation; removal of the carbon monoxide formed and replacement by a charge of fresh carbon dioxide will result in a further evolution of carbon monoxide until equilibrium is again attained. Eventually when all the "active sites" on the surface have been converted to "surface oxide," no further reaction occurs. When the reaction temperature is raised above 500°C the second equilibrium stage assumes predominance and gasification of carbon takes place from the graphite surface. The rate of gasification increases with increasing reaction temperature but eventually is limited by the condition where the rate of diffusion of reactant gas into the graphite mass is slower than the rate of reaction of gas with the accessible surface. This diffusion effect operates with all graphite-gas reactions even at low reaction temperatures. An illustration of this phenomenon at temperatures just above 500°C has been given for the reaction of carbon dioxide with a non-graphitizing carbon of very low porosity with respect to the reactant gas (*34*). When the build-up of carbon monoxide is sufficiently large the reverse of the second equilibrium stage may occur and carbon is deposited by a disproportion process. This is undesirable where graphite is used as a

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structural or moderator material, as it carbon mass transfer may adversely affect the workings of the system. Often the carbon formed in the gas phase is eventually deposited in areas where gas turbulence is a minimum. The disproportionation is often catalyzed by impurities in the graphite and deposits will thus tend to build up at these points on the lattice.

Similar considerations of carbon-oxygen artifacts result from the reaction of water with graphite. In the case of hydrogen-graphite interaction, a wide range of hydrocarbon material is produced although the rate of reaction is several powers of ten slower than the oxygen-graphite reaction under comparable conditions.

Reactions between graphite and gases are further complicated when considerations of radiation-induced reactions are superimposed on the purely thermal conditions. A considerable amount of work has been carried out in this connection; the primary stages in the predominant free radical reaction probably consist of radiation-induced homolyses of the gaseous reactants. Surface topography studies on neutron-damaged graphites indicate that subsequent thermal reactions with carbon dioxide occur at the Frenkel defects of the lattice (*31*).

The temperature for onset of gasification of graphite in carbon dioxide is lowered by the addition of metal impurities (*35*). In contrast, inhibition of gasification is obtained by the addition of traces of metallic borates and phosphates to the graphitic material before reaction. The mechanism of this inhibition is not well defined but must involve blockage of defect sites in the graphite structure by the inhibiting ions, as a reduction in reaction rate may also be induced by high temperature "healing" of lattice dislocations. A discussion of some of these considerations has been given by P. L. Walker (*36*).

Uses and Future Applications

Many novel and varied uses have been suggested for graphite in chemical and industrial processes. The application of graphite, in bulk or dispersion, as a lubricant is well known and considerable controversy and misconception about the mechanism of its action is still apparent (*37*). The older theory supposes that dispersed graphite acts as a solid lubricant between two sliding metal surfaces, owing to its anisotropic character; consequently, shearing takes place between the layer planes of aggregates of orientated crystallites. In the opposing adsorption theory (*38*) abrasion of crystallite edges is minimized by the cushioning presence of water vapor and cases of graphite brush failure under low pressure conditions have been cited to support this contention. A reconciliation between the opposing theories has been advanced by Braithwaite (*39*) who showed that the two theories are based in the first case on the application of graphite containing orientated groups of crystallites, while in the second case disorientated material is considered where the presence of adsorbed water films would be vital to the functioning of the system. Logically therefore graphite as solid or colloid will act as an effective lubricant only if the cleavage forces are parallel to the major axis of the graphite crystallites. Examples of the use of graphite as a lubricant are to be found in the airplane and missile fields, internal combustion engine, electric motors, chemical and gas systems which do not allow easy entry, flow, or retention of liquid lubricant.

The electrical conductivity of graphite is useful where electrodes are required having a high resistance to oxidation. Dispersed graphite can also be applied as thin conducting films as in the manufacture of resistors, electronic and cathode-ray tubes and radiation counters.

The industrial advent of an economic advanced gas-cooled nuclear reactor in the United Kingdom has reinforced the demand for graphite as a fast-neutron moderating material. In this case, together with the use of graphite for refractory containers and as mercury vapor rectifier anodes, the residual gas content of the material must be lowered appreciably. Any adventitious liberation of hydrogen or carbon monoxide would have deleterious effects on the long term operation of the system. The use of graphite for constructing heat exchangers, superior from the corrosion fouling and constructional jointing aspects, has not yet been fully developed. Pyrolytic graphite has already been studied for application to rocket nose cones and exhaust nozzles. Little work has been done on the industrial applications of compounds of graphite, although the use of graphite oxide as an additive for rocket propellants has been patented (*40*).

Recently the use of graphite thermocouples has been suggested for high temperature measurement (*41*).

Conclusions

Graphite, the anisotropic allotrope of carbon, has been shown to have many varied properties and uses. It has always been a challenge to the chemist and technologist, but it is becoming more and more apparent that the "black-art" is finally being mastered. Eventually it should be possible to produce "custom-built" graphite forms having chemical and physical properties appropriate to the application in mind.

Acknowledgment

We wish to thank Mr. R. L. Bond (British Coal Utilisation Rearch Association) and Dr. E. R. Braithwaite (Acheson Colloids Ltd.) for helpful advice during the preparation of the manuscript. We also thank the British Coal Utilisation Research Association and the United Kingdom Atomic Energy Authority for permission to publish the photomicrograph of artificial graphite.

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The Flash of Genius, 14

The Positron: C. D. Anderson

The duality of particles in nature—and hence the theory of anti-matter—was really established with the discovery of the positron in 1932. The discovery had been recognized but the significance not realized after the identification of the proton and electron in the latter part of the 19th century and the early part of the 20th. This *new* duality of particles is termed "particle twins," i.e., they are oppositely charged particles which have the same properties.

The very idea of the existence of any charged particle, other than the proton (+) and the electron (−), was inconceivable to most of these earlier scientists. Dirac[1] in 1928, had produced a brilliant treatment of the application of the quantum theory to the electron for the equation which he derived successfully collated and unified a variety of diverse ideas and calculations. Hans Bethe called it "the greatest paper of our century." But W. Pauli[2] concluded that even though the Dirac equation was a wonderful contribution to physics, it must be erroneous because it entailed the existence of positive electrons.

Experimental evidence for the positron was obtained from "fog tracks" produced in a cloud chamber. The length of these tracks, their width, branching, and direction of curvature are all clues to the nature of the particle that produces them. Over a period of several years nuclear scientists had been observing some "fog tracks" that seemed to be the correct type to have been caused by electrons but their curvature was in the wrong direction. These tracks were commonly referred to as "curving the wrong way," "moving backward," "falling back into the source," etc.[3] Such tracks were also often referred to as "dirt tracks" or just spurious. In this hostile atmosphere, C. D. Anderson proposed his hypothesis "I must assume a particle the mass of an electron but of positive charge." He published his conclusion first in a note[4] as follows:

"Up to the present a positive electron has always been found with an associated mass 1850 times that associated with the negative electron. In measuring the energies of charged particles produced by cosmic rays some tracks have recently been found which seem to be produced by positive particles, but if so the masses of these particles must be small compared to the mass of the proton. The evidence for this statement is found in several photographs, three of which are discussed below.

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"In one instance, in which a lead plate of 6 mm thickness was inserted in the cloud-chamber, tracks of a particle were observed above and below the lead. The curvature due to the magnetic field was measurable both above and below the lead. There are the following alternative interpretations:

A positive particle of small mass penetrates the lead plate and loses about two thirds of its energy; or

Two particles are simultaneously ejected from the lead, in one direction a positive particle of small mass, in the opposite direction an electron; or

An electron of about 20 million volts energy penetrates the lead plate and emerges with an energy of 60 million volts, having gained 40 million volts energy in traversing the lead; or

The chance occurrence of two independent electron tracks in the chamber, so placed as to give the appearance of one particle traversing the lead plate.

"In another instance two tracks of opposite curvature appear below the lead. The alternate interpretations are:

A positive particle of small mass and an electron emerging from the same point in the lead; or

A positive particle of small mass strikes the lead and rebounds with a loss in energy; or

An electron of about 20 million volts energy strikes the lead and rebounds with 30 million volts energy; or

The chance occurrence of two independent electron tracks.

"In the third instance two tracks appear below the lead plate. The alternative interpretations are:

A positive particle of small mass and another positive particle emerge from the same point in the lead; or

A 4 million volt electron rebounds from the lead producing the second track; but here a difficulty is met with, since a change in the sign of the charge would have to be assumed to take place in the rebound of the electron; or

The chance occurrence of two independent tracks.

"For the interpretation of these effects it seems necessary to call upon a positively charged particle having a mass comparable with that of an electron, or else admit the chance occurrence of independent tracks on the same photograph so placed as to indicate a common point of origin of two particles. The latter possibility on a probability basis is exceedingly unlikely.

"The interpretation of these tracks as due to protons, or other heavier nuclei, is ruled out on the basis of range and curvature. Protons or heavier nuclei of the observed curvatures could not have ranges as great as those observed. The specific-ionization is close to that for an electron of the same curvature, hence indicating a positively-charged particle comparable in mass and magnitude of charge with an electron."

The next year he published a more detailed report[5]:

"On August 2, 1932, during the course of photographing cosmic-ray tracks produced in a vertical Wilson chamber (magnetic field of 15,000 gauss) designed in the summer of 1930 by Professor R. A. Millikan and the writer, tracks were obtained which seemed to be interpretable only on the basis of the existence in this case of a particle carrying a positive charge but having a mass of the same order of magnitude as that normally possessed by a free negative electron. Later study of the photograph by a whole group of men of the Norman Bridge Laboratory only tended to strengthen this view. The reason that this interpretation seemed so inevitable is that the track appearing on the upper half of the figure cannot possibly have a mass as large as that of a proton for as soon as the mass is fixed the energy is at once fixed by the curvature. The energy of a proton of that curvature comes out 300,000 v, but a proton of that energy according to well established and universally accepted determinations has a total range of about 5 mm in air while that portion of the range actually visible in this case exceeds 5 cm without a noticeable change in curvature. The only escape from this conclusion would be to assume that at exactly the same instant (and the sharpness of the tracks determines that instant to within about a fiftieth of a second) two independent electrons happened to produce two tracks so placed as to give the impression of a single particle shooting through the lead plate. This assumption was dismissed on a probability basis, since a sharp track of this order of curvature under the experimental condition prevailing occurred in the chamber only once in some 500 exposures, and since there was practically no chance at all that two such tracks should line up in this way. We also discarded as completely untenable the assumption of an electron of 20 million v entering the lead on one side and coming out with an energy of 60 million v on the other side. A fourth possibility is that a photon, entering the lead from above, knocked out of the nucleus of a lead atom two particles, one of which shot upward and the other downward. But in this case the upward moving one would be a positive of small mass so that either of the two possibilities leads to the existence of the positive electron.

"In the course of the next few weeks other photographs were obtained which could be interpreted logically only on the positive-electron basis, and a brief report was then published with due reserve in interpretation in view of the importance and striking nature of the announcement."

[5] ANDERSON, C. D., *Phys. Rev.*, 43, 492–4 (1933).

. . . an informed citizen should be conversant with the larger principles of science, the dynamic potential of scientific research, the main contemporary currents of scientific effort and their relationship to social forces.

With such an understanding, an intelligent citizen can make intelligent judgments between good and bad policy on scientific and technical matters. Without it, he can hardly participate fully in a scientific democracy.

GLENN T. SEABORG
Chairman, AEC

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Ionic and Molecular Halides of the Phosphorus Family

At the present time sufficient information has appeared in the literature regarding ionic and molecular halides of the Group V elements (P, As, Sb and Bi) to warrant a summary discussion to ascertain whether some semblance of correlation exists. If so, perhaps possible directions for future research may suggest themselves.

Many of the investigations, by necessity, have been concerned with the synthesis and identification of ionic and molecular halides and a study of their simple chemistry. There also have been a smaller number of more detailed investigations concerned with structural aspects of the halides. Little thermodynamic data is available and studies of reaction mechanisms are almost nil. As will be seen, one reason for the lack of investigations concerned with more elegant experimentation, aside from air and moisture sensitivity, is the existence of a multitude of structural states for these halides and the complexity of their interconversions.

The Pentahalides

While all the trihalides of phosphorus, arsenic, antimony and bismuth are known, not all of the pentahalides have been prepared. The most recent preparation is that of BiF_5 (*1*). The melting points and boiling points of the known pentahalides are listed in Table 1. In addition the mixed pentahalides,

Table 1. The Pentahalides: Melting and Boiling Points (°C).[a]

	F_5		Cl_5		Br_5	
	Mp	Bp	Mp	Bp	Mp	Bp
P	−93.7	−84.5	167(subl.)	...[b]	<100	dec.
As	−79.8	−53.2	...	...	...	...
Sb	+7	+150	+5	~140	...	...
Bi	151[c]	230	...	...	...	...

[a] Reference (*13*).
[b] ..., unknown; all iodides are unknown.
[c] Reference (*1*).

$PFCl_4$ (*2*), PF_2Cl_3 (*3*), PF_3Cl_2 (*4*), PBr_4F (*5*) and PBr_2F_3 (*6*) have been reported in molecular form. Some of the chlorofluorides of antimony (V) have been reported (*7*). None of the mixed pentahalides of arsenic have been isolated.

Structural investigations on the pentahalides have demonstrated the presence of a trigonal bipyramidal configuration for the compounds listed in Table 2.[1] While PCl_5 and PBr_5 possess trigonal bipyramidal structures in the vapor, they are ionic in the solid, PCl_4^+-PCl_6^- (*8*) and PBr_4^+ Br^- (*9*) respectively. Transport studies on solutions of PBr_5 in acetonitrile (*10*) support the presence of PBr_4^+ PBr_6^- rather than PBr_4^+ Br^-. The latter, if so, is the only example of the PBr_6^- ion.

In addition to the above pentahalides, the solids, P_2Cl_9F (*11*) and P_2Cl_9Br (*12*), have been reported and the structure, $PCl_4^+PCl_5X^-$ (X = F or Br), postulated. Recently powder pattern data suggest BiF_5 to have a structure analogous to the body centered tetragonal α polymorph of UF_5 (*1*).

Dissociation of the Pentahalides. The tendency to dissociate to the trihalide and halogen is shown to a large extent by PBr_5, to a lesser extent by the pentachlorides of P and Sb and least by the pentafluorides (*7*, *13*), although measurements have shown that the vapor over liquid BiF_5 at 174° is almost entirely fluorine (*1*).

Thermodynamic data on the dissociation of the pentahalides

	ΔH kcal mole^{-1}	Ref.
$PCl_5(g) = PCl_3(g) + Cl_2(g)$	21.3	(14)
$PBr_5(s) = PBr_3(g) + Br_2(g)$	26.5	(15)
$PCl_4F(g) = PCl_2F(g) + Cl_2(g)$	11(indirect)	(11)
$SbCl_5(g) = SbCl_3(g) + Cl_2(g)$	16.3	(16)

suggest that substitution of a fluorine in place of a chlorine atom lowers the average P — Cl bond energy; however, PCl_2F_3 shows no dissociation up to 150°. Payne suggests (*7*) intramolecular elimination of chlorine atoms in adjacent positions is more facile, thus explaining the ready dissociation of PCl_5, $SbCl_5$ and PCl_4F compared to PCl_2F_3 where the chlorine atoms are in polar positions.

Freezing point diagrams (*17*) of the systems MX_3 — X_2 (where X = Cl, Br or I) give no evidence of pentahalide formation for pentahalides which are not listed in Table 1. The complex ion $[SbBr_6]^-$ exists; however, evidence indicates that it is a polybromide complex of tripositive antimony (*18*).

Table 2. Structural Data on Pentahalides, Bond Length, Å.

	Exptl.[a]	Theory[b]		Exptl.	Theory
PF_5 (*g*)	1.57	1.59	$SbCl_5$ (*g*)	2.31 *e* 2.43*a*	2.38
PCl_5 (*g*)	2.04*e* 2.19*a*	2.04	$SbCl_5$ (*s*)	2.29*e* 2.34*a*	2.38
PCl_2F_3 (*g*)	1.59*e* 2.05*a*	1.59 2.04	Me_3SbCl_2 (*s*)	2.49[c]	
			Me_3SbBr_2 (*s*)	2.63[c]	2.53

[a] *e*, equatorial; *a*, apical.
[b] Corrected for electronegativity differences.
[c] Error uncertain.

Presented as part of the Symposium on the Chemistry of Group V Elements, sponsored by the Division of Inorganic Chemistry, and the 142nd Meeting of the American Chemical Society, Atlantic City, New Jersey, September 1962.

[1] Except for solid $SbCl_5$ the structures are taken from Sutton, L. E., edit., "Tables of Interatomic Distances and Configuration in Molecules and Ions," The Chemical Society, Burlington House, London, 1958. The solid $SbCl_5$ structure comes from Ohlberg, S. M., *J. Am. Chem. Soc.*, **81**, 811 (1959).

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Recently a study of the systems $AsCl_3$-Cl_2, $AsBr_3$-Br_2 and $SbBr_3$-Br_2 was carried out to ascertain whether equilibrium pentahalide formation existed in the liquid phase (*19*). No tendency for formation of either $AsCl_5$ or $SbBr_5$ was present but small negative deviations from ideal behavior were observed in the $AsBr_3$-Br_2 system, suggesting weak solvation.

The nonexistence of $AsCl_5$ is not thought to be directly related to the rarity of the pentacoordinated state since elements in the same row experience a similar reluctance to exist in the higher oxidation states; for example, perbromates do not exist while perchlorates and periodates are common.

Association of the Pentahalides. Some of the pentahalides give evidence of being polymeric in the vapor. Thus a mass spectral investigation of PCl_5 (*20*) showed peaks at mass numbers indicating the parent ion, $P_2Cl_{10}^+$. Similar results (*11*) on the vapor of PCl_4^+ PCl_5F^- at room temperature indicate the molecular specie, P_2Cl_9F. Structures containing four membered halogen bridges have been suggested. Kolditz (*12*) has prepared a related solid, PCl_4^+ PCl_5Br^-, but has no data on the vapor.

SbF_5 appears more highly associated in the vapor than the phosphorus compounds so far investigated. Values of the molecular weight as high as 1230 (SbF_5 = 217) just above the boiling point have been obtained (*15*). Liquid SbF_5 is also associated as ^{19}F NMR measurements have shown (*21*). The data support a chain polymer character involving adjacent fluorine atoms acting as bridging groups (Fig. 1). Cryoscopic measurements also suggest association of PCl_5 in CCl_4 solution (*22*).

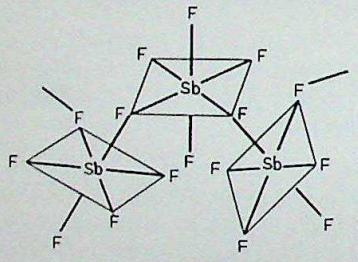


Figure 1. Structure of SbF_5 (l).

The Trigonal Bipyramidal Problem

An examination of the data in Table 2 shows that both PCl_5 and $SbCl_5$ have two different bond distances, the polar chlorines being longer than the equatorial chlorines. With PF_5 this is not so. Here only one distance is reported. The latter is in apparent agreement with ^{19}F NMR studies which show only one type of fluorine and the absence of intermolecular fluorine exchange (*23, 24*). Recently the ^{19}F spectrum of AsF_5 was obtained (*25*) and exhibited a single broadened peak. The broadening was attributed to colloidal impurities in the sample.

On purely geometrical considerations one would expect nonequivalence of bonds for the coordination number of five, since five points cannot be placed in equivalent positions on the surface of a sphere (disregarding the case where they occupy equidistant points on a great circle). ^{13}C NMR measurements on $Fe(CO)_5$, which also has the trigonal bipyramidal structure, again show only one type of carbon (*26*). The problem at present is unresolved.

Results of exchange experiments (*27*) on chlorine and PCl_5 in CCl_4 solution have been interpreted to show that three chlorine atoms react more rapidly than the other two. A transition state involving addition of a halogen molecule primarily in the equatorial plane is suggested. The latter results are at variance to expectations if one assumes that shorter bond distances imply greater bond strength and that greater bond strength is the controlling factor in comparing reactivity of the apical and equatorial positions. In PCl_5, mentioned earlier, the polar bonds are longer. The same is true for $SbCl_5$. However, as Kolditz and Hass point out (*22*) the exchange mechanism most likely is more complicated than the authors (*27*) assume. In CCl_4, for example, cryoscopic studies (*22*) indicate that PCl_5 is associated.

On studying the exchange of radioactive chloride ion (tetraethylammonium chloride) with PCl_5 dissolved in CH_3CN, Kolditz and Hass (*22*) found three chlorines exchanging more rapidly than the other two. However, as the authors mention (*28*) PCl_5 in CH_3CN exists in the ionic form, PCl_4^+ PCl_6^-. The exchange results, hence, reflect the instability of the PCl_6^- ion compared to that of the PCl_4^+ ion.

Mixed Pentahalides

The mixed pentahalides, $PFCl_4$, PF_2Cl_3, PF_3Cl_2 and PBr_4F are extremely interesting. On preparation they usually form as molecular liquids. On standing though they transform in a period of days to solid ionic modifications (*3*). Both modifications are moisture sensitive. The resulting structures are formulated as PCl_4^+ F^- for solid $PFCl_4$ (*2*), PCl_4^+ PF_6^- for solid PF_3Cl_2 (*29*) and PBr_4^+ F^- for solid PBr_4F (*5*) (evidence for the structure of solid PF_2Cl_3 is lacking). Most of the evidence to date for the ionic structures other than simple physical properties results from conductance and molecular weight studies of solutions of the salts in solvents such as acetonitrile, nitrobenzene or arsenic trifluoride. X-ray powder data has also been used.

The mixed pentahalides having the empirical formulas, PF_3Br_2, AsF_3Cl_2, $SbCl_4F$ and $SbCl_2F_3$, have also been prepared but except for SbF_3Cl_2 usually form as the solid ionic products. Work on molecular forms, if they do exist, has not been carried out to any degree. Respectively, they have been formulated as PBr_4^+ PF_6^- (*30*), $AsCl_4^+$ AsF_6^- (*31*), $SbCl_4^+$ F^- (*32*) and $SbCl_4^+$ SbF_6^- (*33*). If one examines the vapor of these substances, perhaps evidence for a molecular form may result. Table 3 summarizes the various forms.

Preparation of Mixed Pentahalides. The molecular pentahalides are usually prepared by the direct addition of the appropriate halogen to the trihalide as illustrated by the following reactions.

$$SbF_3 + Cl_2 + \xrightarrow[8\text{ hrs}]{80^\circ} SbCl_2F_3 \rightleftarrows SbCl_4^+SbF_6^- \text{ (mp 68°)}$$

$$PF_3 + Cl_2 \xrightarrow{25^\circ} PF_3Cl_2 + PCl_4^+PF_6^- + PCl_4^+F^-$$

$$AsF_3 + Cl_2 \xrightarrow[4\text{ hrs}]{0^\circ} AsCl_4^+AsF_6^- \xrightarrow{\Delta} AsF_3 + Cl_2(\text{no } AsCl_4F)$$

The rate is much more rapid in the case of the

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PF_3-Cl_2 reaction (*4*) than the SbF_5-Cl_2 reaction (*33*) such that ionic products form along with PF_3Cl_2; whereas, the rate of formation of $SbCl_4^+$ SbF_6^- apparently is sufficiently slower than the rate of formation of $SbCl_2F_3$ that the latter is readily isolated. One may obtain PF_3Cl_2 in pure form by performing the chlorine addition at −125° (*3*). Reaction proceeds at a lively rate to yield PF_3Cl_2 but the rate of formation of ionic products is negligible at this temperature.

The corresponding AsF_3-Cl_2 reaction (*31*) proceeds favorably at 0°C yielding $AsCl_4^+$ AsF_6^- directly. The fact that no molecular AsF_3Cl_2 was formed reflects the instability of the pentavalent state for arsenic.

A further preparative method used to form other molecular species, at least in the case of phosphorus, is to heat the ionic solids. PCl_4^+ PF_6^- may be obtained conveniently (*29*) by the fluorination of PCl_5 in $AsCl_3$ at 25° using the proper amount of AsF_3. Heating the latter ionic product suspended in $AsCl_3$ yields molecular PCl_4F which is a liquid (*2*). Gaseous PF_5 and PF_3Cl_2 are also produced but are easily fractionated off. PCl_4F may also be produced by the low temperature addition of chlorine to $PFCl_2$ (*3*). The complexity and interrelations involved in these reactions are summarized below.

$$\begin{array}{l} PF_5 + AsCl_3 \qquad\qquad PCl_4^+F^- \quad (20\%) \\ \qquad\uparrow \qquad\qquad\qquad\uparrow \\ \qquad\uparrow \xrightarrow{80°} PF_5 + PCl_4F + PF_3Cl_2 \\ \qquad\uparrow AsF_3 \quad \uparrow AsCl_3 \\ AsF_3 + PCl_5 \xrightarrow[25°]{AsCl_3} PCl_4^+PF_6^- + AsCl_3 \qquad (29) \\ \qquad\qquad \overset{\Delta}{\underset{8\ hr}{\downarrow}} \quad \downarrow CCl_4 \\ PCl_4^+PCl_5F^- + PF_5 + PF_3Cl_2 + PCl_4^+F^- \qquad (11) \end{array}$$

$$PCl_3 + Br_2 \xrightarrow{AsCl_3} PCl_4^+PCl_5Br^- \xrightarrow{AsF_3} PCl_4^+PF_6^- \qquad (12)$$

Table 3. Formulas of Mixed Pentahalides

Molecular	Mp (°C)	Bp (°C)	Ionic	Mp (°C)
$PFCl_4$	−63	67	$PCl_4^+F^-$	177
PF_2Cl_3	−63			
PF_3Cl_2	−124	8	$PCl_4^+PF_6^-$	subl., 135 (dec.)
PBr_4F			$PBr_4^+F^-$	87
PBr_2F_3	−20		$PBr_4^+PF_6^-$	subl., 135
			$AsCl_4^+AsF_6^-$	~160
			$SbCl_4^+F^-$	
SbF_3Cl_2			$SbCl_4^+SbF_6^-$	~ 68

Halide Ion Stability (Pentavalent)

Table 4 lists the known ions found in solid complexes containing the Group V elements in the pentavalent state. It has been suggested that the complex ion $SbCl_6^-$ contains antimony in the tri and pentavalent state (*34*). The latter would account for the observed diamagnetism.

In addition to containing different halogens, the pentahalides also form ionic complexes containing two different Group V elements. Thus PCl_5 and $SbCl_5$ react directly on heating (*35*) and form PCl_4^+ $SbCl_6^-$ (*36*). Such reactions yield information on the relative stability of ion species. Assuming that crystal lattice variations are not controlling stability one would predict that either $SbCl_6^-$ is more stable than PCl_6^-, or PCl_4^+ is more stable than $SbCl_4^+$, or both.

Looking at the existence of complexes, many more are known containing the PCl_4^+ ion compared to those containing $SbCl_4^+$ as seen in Table 5. No complexes containing BiX_4^+ are known. However, the criterion of larger number of complexes reflecting stability has been shown in the past not to be the best but may only indicate the relative amount of research devoted to more readily available compounds.

As shown in Table 4 MX_6^- ions exist only for the known pentahalides. As with MX_4^+ ions indications of relative stability are few. Some of the more pertinent considerations are discussed below.

In a recent study $SbCl_5$ (*37*) has been found to be a stronger acceptor molecule toward pyridine than PCl_5 and that phosphorus(V) fluorochlorides are stronger than PCl_5. Disregarding variations in crystal lattice energy and assuming acceptor strength parallels ion stability, the $SbCl_6^-$ would be more stable than PCl_6^- and fluoride anions would be more stable than the corresponding chloride containing anions. The order of thermal stability (*38*) of the complexes,

$$SF_4 \cdot SbF_5 > SF_4 \cdot AsF_5 > SF_4 \cdot BF_3,$$

is also in the same direction. Evidence (*39*) indicates that the latter complexes possess onium structures. As such, SbF_6^- is indicated to be more stable than AsF_6^-.

However, much more work is needed to firmly establish the relative importance of various quantities in determining ion stability in this series. One factor that should not be neglected is the variation in crystal lattice energy. These variations must enter into considerations of this type and have been neglected only because of the difficulty in assessing their importance.

To ascertain ion stability quantitatively, thermodynamic data suggested by the following cycle is needed (MPX_6 is used as an example). Little such data is available at present.

Table 4. Halide Ions of Pentavalent P, As, Sb and Bi

	PF_6^-
PCl_4^+	PCl_6^-
PBr_4^+	AsF_6^-
$AsCl_4^+$	
	SbF_6^-
$SbCl_4^+$	$SbCl_5^-$ $SbCl_6^-$
	$(SbBr_6^-)^a$ $SbBr_6^-$
$BiCl_4^+$	BiF_6^-

[a] $(SbBr_6^-)$, thought to be a polybromide complex of trivalent Sb.

Table 5. Complexes Indicated to Contain the MX_4^+ Ion.

PCl_4^+[a]	$AsCl_4^+$	$SbCl_4^+$	PBr_4^+
PF_6^-	AsF_6^-	SbF_6^-[c]	PF_6^-
F^-		F^-	F^-
PCl_6^-	PCl_6^-		
$SbCl_6^-$	$SbCl_6^-$		Br^-
BCl_4^-			
$AlCl_4^-$	$AlCl_4^-$		
$GaCl_4^-$[b]	$GaCl_4^-$		
ICl_2^-			
$FeCl_4^-$	$FeCl_4^-$		
$AuCl_4^-$	$AuCl_4^-$		

[a] Partial list of PCl_4^+ but quite a complete list for the other MX_4^+ ions. References (*7*) and (*13*).
[b] R. R. Holmes, *J. Inorg. Nucl. Chem.*, 14, 179 (1960).
[c] Reference (*33*).

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$$P(s) + 5/2\ X_2(g) \xrightarrow{\Delta H_f} PX_5(g)$$

$$PX_5(g) \xrightarrow{A} PX_6^-(g)$$

$$1/2\ X_2(g) \xrightarrow{1/2\ D} X(g) \xrightarrow{F} X^-(g)$$

$$M(s) \xrightarrow{S} M(g) \xrightarrow{I} M^+(g)$$

$$PX_6^-(g) + M^+(g) \xrightarrow{U} MPX_6(s)$$

$$P(s) + 3X_2(g) + M(s) \xrightarrow{\Delta H} MPX_6(s)$$

$$\Delta H = S + I + 1/2\ D + F + \Delta H_f + A + U$$

When the discussion centers on two related complexes involving the same cation and halogen and also assumes that variations in U are not highly significant, then the relative stability is related to factors making up variations in ΔH_f, the heat of formation of the pentahalide, and A, a quantity related to the acceptor strength of the pentahalide molecule.

Acceptor Character of PF_xCl_{5-x}. The ordering of election pair acceptors, $PCl_3F_2 > PCl_4F > PCl_5$, toward pyridine (*37*) in line with electronegativity considerations is opposite to that of the boron halide series, $BBr_3 > BCl_3 > BF_3$ (*40*). In the boron halide series variations in degree of pi bonding have been advanced to explain the ordering. Apparently the pentahalides may coordinate with little disturbance to the degree of pi bonding present.

As discussed elsewhere (*37*) the latter seems reasonable. In the boron trihalide molecules, boron can enter into pi bonding with its one p orbital. On coordination such stabilizing bonding is largely destroyed since the p orbital now enters into bonding with the incoming group. For the phosphorus pentahalide molecules, if phosphorus does enter into pi bonding, it may do so with up to four of its d orbitals. On coordination, the degree of pi bonding need not be disturbed to as large a degree as it does in the boron halide series. There remain three d orbitals of phosphorus yet available for pi interaction in the coordinated molecule (Fig. 2).

Halide Ion Stability (Trivalent)

As with the pentavalent state, a variety of halide complexes are known for trivalent Group V elements (*7*, *13*). Table 6 lists the common types of ions that have been reported for each element. None are known for phosphorus. Here again no comparative evidence of the relative stability of the various anions is available other than the apparent increase in such complexes in going to the heavier elements.

The latter parallels what is known concerning the acceptor character of the trihalides (Table 7). Phosphorus trihalides act as very weak acceptor molecules and form readily dissociable adducts with $(CH_3)_3N$ (*41*) while adducts of the heavier trihalides give indications of being more stable (*42*).

Table 6. Halide Ions of Trivalent P, As, Sb and Bi

AsF_4^-		
$AsCl_4^-$		
$AsBr_4^-$	$AsBr_5^=$	
SbF_4^-	$SbF_5^=$	
$SbCl_4^-$	$SbCl_5^=$	$SbCl_6^=$
BiF_4^-	$BiF_5^=$	$BiF_6^=$
$BiCl_4^-$	$BiCl_5^=$	$BiCl_6^=$
$BiBr_4^-$	$BiBr_5^=$	$BiBr_6^=$

Table 7. Trihalide Molecular Complexes

Donor[a]	Acceptor[b]	Complex[c]
$PF_3 \cdot BH_3$		
$PCl_3 \cdot GaCl_3$	$PCl_3 \cdot AsMe_3$	
$PCl_3 \cdot BBr_3$	$PF_3 \cdot NMe_3$	$(X_3P)_2PtCl_2$
$PBr_3 \cdot BBr_3$	$PCl_3 \cdot NMe_3$	$Ni(PX_3)_4$
$2PCl_3 \cdot B_2Cl_4$	$PBr_3 \cdot NMe_3$	$Ni(CO)_3SbCl_3$
(As, Sb, Bi non-existent)	(As, Sb, Bi, a variety)	$Fe(CO)_3(SbCl_3)_2$

[a] All the known donor complexes.
[b] All known acceptor complexes of PX_3. The list for As, Sb and Bi is extensive.
[c] See reference (*7*) and (*13*).

Obviously this comparison is even more premature than in the case of the pentavalent state. In fact the existence of simple MX_4^- ions has yet to be observed in the crystalline state. Thus, single crystal X-ray studies (*43*) have shown that $KSbF_4$ is most likely tetrameric (Fig. 3). It contains pentacoordinated antimony in a distorted tetragonal pyramidal structure.

Both K_2SbF_5 (*44*) and $(NH_4)_2\ SbCl_5$ (*45*) possess a related structure. Figure 4 shows the structural data for K_2SbF_5. Such a structure might be imagined as a distorted octahedral structure with one of the positions occupied by a lone pair of electrons, the lone pair causing repulsion of the four ligands *cis* to it

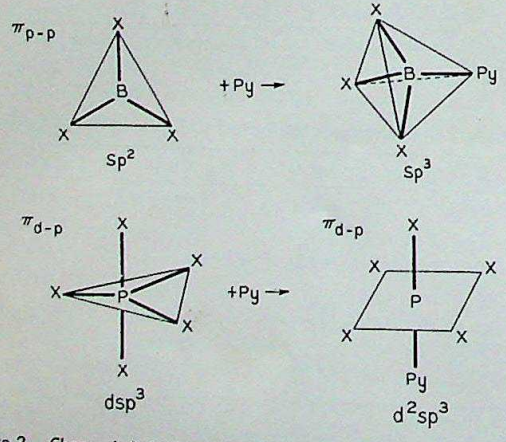


Figure 2. Change in hybridization and pi bonding on coordination for BX_3 and PX_5.

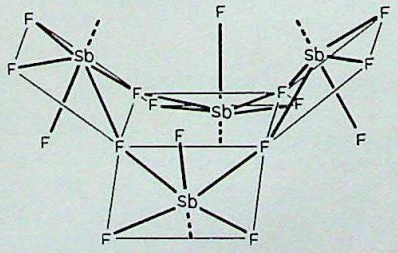


Figure 3. Structure of $KSbF_4$.

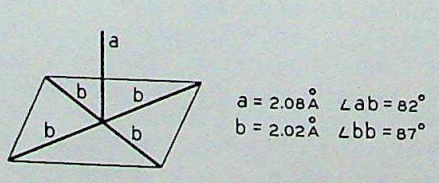


Figure 4. Structure of K_2SbF_5

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(*46*). Since the bonding in the latter structure would involve hybridization approximating sp^3d^2, one would predict that simple ions of the type MX_4^- (imagined as formed by halide removal from $MX_5^=$ and resulting in sp^3d bonding) should have a distorted trigonal bipyramidal structure similar to their isoelectronic counterpart, SF_4 (Fig. 5).[2] The antimony environment in KSb_2F_7 (*47*) is somewhat analogous (Fig. 6). X-ray data on KSb_4F_{13} (*48*) show fluoride ions solvated by four SbF_3 molecules (Fig. 6).

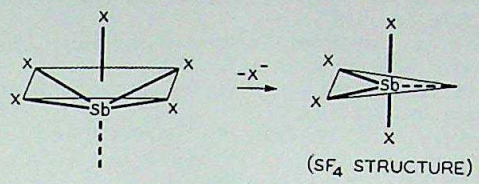


Figure 5. Postulated structure of MX_4^-.

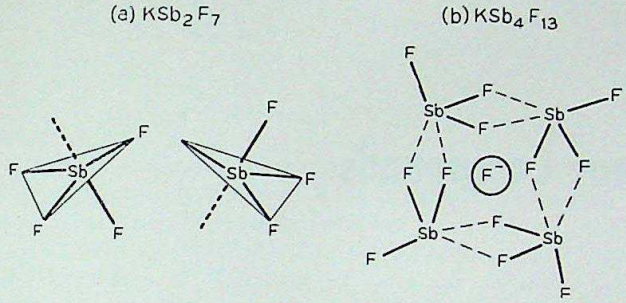


Figure 6. Structures of (a) KSb_2F_7 and (b) KSb_4F_{13}.

Commenting again on molecular trihalide complexes, phosphorus trihalides have been found to function as weak donors (*49–52*) as well as weak acceptors (Table 7). Simple donor action has not been observed in the heavier trihalides. The third column lists complexes which contain multiple bonding where both donor and acceptor action most likely takes place to some degree.

Current Problem

In addition to the many problems which may have suggested themselves in the above presentation, two others worthy of mention are the preparation of stibonitrilics and the use of ionic and mixed halides as controlled halogenating agents. By suitable choice of reaction conditions, one might prepare $(SbNCl_2)_x$ analogous to the phosphonitrilic compounds. In view of the proposed mechanism (*53*) for the formation of phosphonitrilics, direct interation of $SbCl_5$ and NH_4Cl is doubtful.

$$PCl_5 + NH_4Cl \rightarrow \underset{\text{(unstable)}}{NH_4PCl_6} \xrightarrow{-HCl} NH=PCl_3 \xrightarrow{-HCl} (PNCl_2)_n$$

Fireman (*54*) in 1904 studied the latter reaction using NH_4Cl as well as other metal chlorides and obtained the very stable $SbCl_6^-$ at 200°. Decomposition resulted at higher temperatures.

Thus the synthetic route chosen should avoid the formation of $SbCl_6^-$ as an intermediate. One suggested process is to use a base of appropriate strength to complex the $SbCl_5$ and serve as a solvent. Other routes might be imagined.

$$3B + B \cdot SbCl_5 + NH_4Cl \rightarrow (SbNCl_2) + 4BH^+Cl^-$$

With regard to halogenation reactions some of the ionic halides might prove to be a controlled source of halogenating agent and accordingly moderate a reaction which might otherwise proceed vigorously if a halogen were used directly. On the other hand certain halogenations proceed to a greater degree when mixtures of halides are used. Thus, SbF_3 fluorinates B-trichloroborazine to B-monofluorodichloroborazine; whereas, a mixture of SbF_3 with $SbCl_5$ yields B-difluoromonochloroborazine (*55*). It may be that an antimonyV chlorofluoride is formed and acts as a more powerful fluorinating agent than the trifluoride. In any event, an investigation of this aspect of these halides would be worthwhile.

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Non-existent Compounds

There exists a large and diverse group of compounds whose structures do not offend the simpler rules of valence, but which nevertheless are characterized by a high degree of instability; in many cases the compounds in question have never been prepared. The purpose of this review is to collect such compounds together and to inquire into the basis of their instability or non-existence, which in some cases is well understood, in others only imperfectly. It is considered that textbooks of chemistry might well pay more attention to this aspect of the subject, since inquiry into the reasons for the non-existence of a particular compound can often be an educationally profitable pursuit. Such compounds constitute a healthy supplement to the diet of well-established compounds usually provided for student consumption.

For the purposes of discussion, the compounds have been divided into a number of classes; in each of these the low stability of the members can usually be traced to one or more common sources, except for the final miscellaneous group.

Class 1

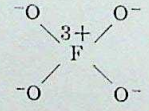
Class 1 compounds are those whose instability is a consequence of the restriction of first-row atoms to a valence octet.

The valence shell of the first row elements can accommodate a maximum of eight electrons in the 2*s* and 2*p* orbitals. It is well known that the formation of more than four covalent bonds by these atoms would necessitate the use of their 3*d* orbitals, and the energy difference between these and the orbitals of the preceding quantum level is so large as to make the promotional energies involved in their use excessively high.

Although Gillespie (*1*) has argued that this factor does not completely exclude the possibility of octet expansion, the use of 3*d* orbitals in stable compounds of first row atoms has never been demonstrated.

Some compounds whose existence might otherwise have been expected, with their stable second row analogues in parentheses, are Na_3BF_6 (Na_3AlF_6), $K_3B(C_2O_4)_3$ ($K_3Al(C_2O_4)_3$), Na_2CF_6 (Na_2SiF_6), NF_5 (PF_5), $NaNF_6$ ($NaPF_6$), OF_4 (SF_4), OF_6 (SF_6).

The non-existence of oxyacids of fluorine such as HFO_4 is almost certainly related to this restriction. Although the FO_4^- ion can be formulated without recourse to fluorine 3*d* orbitals, i.e.,



such a structure is unacceptable (*a*) because of the high formal positive charge on the fluorine atom (which is uniquely more electronegative than oxygen), and (*b*) because in similar but stable ions formed by the other halogens, e.g., ClO_4^-, there is abundant evidence (*2*) that the Cl-O bond has stabilizing multiple-bond character resulting from back-coordination of the lone pair p_π orbitals on the oxygen atoms into the vacant 3*d* orbitals on the chlorine atom. Multiple bonding of this sort cannot occur for fluorine, because of its lack of *d* orbitals of suitable energy.

Class 2

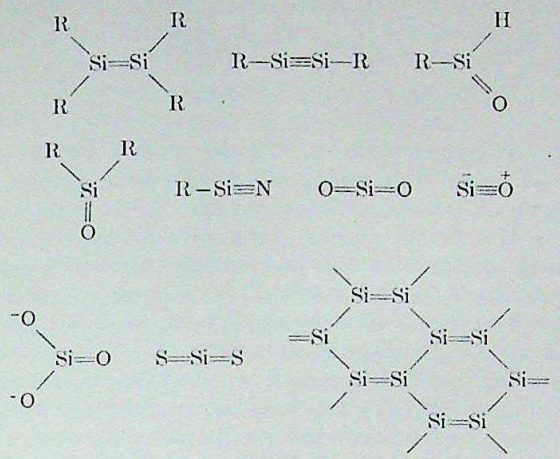
Class 2 consists of compounds whose instability is a consequence of the reluctance of the atoms of the second (and subsequent) rows to form multiple bonds involving $p_\pi - p_\pi$ overlap.

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This is a most marked and widespread phenomenon typified by the following examples from the chemistry of silicon, phosphorus, and sulfur:

Silicon. True iso-structural silicon analogues (formulas shown below) of multiple bonded carbon compounds such as ethylene, acetylene, acetaldehyde, acetone, acetonitrile, carbon monoxide, carbon dioxide, carbon disulfide, the carbonate ion, and graphite, have not been prepared:



If these structures were adopted, then in each case the π-component of the Si-X multiple bond would result from the "sideways" overlap of a silicon $3p_\pi$ orbital with a p_π orbital of the second atom, but in fact the formation of this type of bond is avoided. In many cases, compounds with the same *empirical* formula as the carbon analogue are known, but their structures are always polymerized, in such a way that each $p_\pi - p_\pi$ bond is replaced by a bond of the sigma type.

For example, compounds having the same composition as ethylene and acetylene can be prepared as polymerized solids, i.e., $(SiH_2)_n$ (*3*), and $(SiH)_n$ (*4*); silico-formaldehyde forms a six-fold polymer $(H_2SiO)_6$ (*5*); diethyl silico-ketone a three-fold polymer $(Et_2SiO)_3$ (*6*); and silico-oxalic acid, $(SiOOH)_2$, an insoluble polymerized solid lacking acidic properties (*7*). Similarly SiO_2 (quartz) has a three-dimensional giant lattice (*8*) in which the silicon atoms form four single sigma bonds in contrast to the two C=O double bonds in molecular carbon dioxide; the ion SiO_3^{2-} does not occur (*8*) as a discrete anion like CO_3^{2-}, but in the form of endless polymerized metasilicate chains as in the pyroxene minerals; and SiS_2 also adopts (*9*) a non-molecular chain structure.

Phosphorus. Many of the common compounds of nitrogen (e.g., N_2, N_2O, NO, N_2O_3, NO_2, N_2O_4, N_2O_5, HNO_2, HNO_3) form molecules in which $p_\pi - p_\pi$ bonds are present. Where phosphorus analogues of these molecules are formed, their structures are generally such that this type of bond is absent; the only exceptions are found in such species as P_2 and PO, which occur in the gas phase at elevated temperatures. Thus elemental phosphorus at ordinary temperatures and pressures adopts one of the single-bonded structures exemplified by white phosphorus (P_4) or the more extensively polymerized red and black allotropes; PO (*cf.* NO) exists as a brown polymeric solid $(PO)_n$ (*10*), which becomes molecular only at high temperatures; PO_2 (*cf.* NO_2) is extensively polymerized in the gas phase, its molecular weight lying between 293 and 721, depending on conditions (*11*); and P_4O_6 and P_4O_{10} (*cf.* N_2O_3 and N_2O_5) have the well-known structures related to the P_4 tetrahedron.

Sulfur. The stable forms of elemental sulfur at room temperature and pressure are those which, as in the S_8 molecule, involve S-S single sigma type bonds, in contrast to the π-bonded O_2 and O_3 molecules. S_2 is known in the gas phase at high temperatures, and can be obtained as a purple paramagnetic solid by shock-cooling the vapor to $-196°C$ (*12*). Solid S_2 reverts to single-bonded allotropes even at $-80°C$, and is thus highly unstable.

It should be emphasized here that it is only a particular type of π-bond—that resulting from the overlap of two p_π orbitals—which is so rarely formed by second row atoms. Multiple bonds in which their 3*d* orbitals are used are of widespread occurrence (*2*, *13*) and this fact may be of significance in seeking an explanation of the phenomena discussed in this class. One view, due to Pitzer (*14*), is as follows. The atoms of the second row (and of subsequent rows) all have larger inner electron shells than those of the first row; consequently X-X single bond distances (see Table 1) are all larger for second row atoms because of the increased repulsive forces between the inner shell of one atom and the bond-forming p_x orbital of the other. If a multiple bond is to be formed, the p_y and p_z orbitals must approach sufficiently closely to overlap in "sideways" fashion, and effective achievement of this is prevented by the inner shell $- p_x$ orbital repulsions. This state of affairs is illustrated diagrammatically in Figure 1.

Table 1. X-X Interatomic Distances(Å). (Data from ref. 21, chapter 7.)

C–C	N—N	O–O	F–F
1.54	1.47	1.47	1.42
Si–Si	P–P	S–S	Cl–Cl
2.34	2.20	2.08	1.98

On this basis it can be understood why π-bonds of the $3d_\pi - p_\pi$ type are readily formed by second row atoms, since the lobes of a 3*d* orbital are directed towards the p_π orbital, giving more effective overlap.

An alternative view, for which Mulliken (*15*) has argued cogently, is that the preference of second row atoms for single-bonded structures results from the strengthening of their σ -bonds by *d* orbital hybridization, rather than from any pronounced weakening of their p_π -p_π bonds. Thus the problems cannot at this stage be regarded as completely settled.

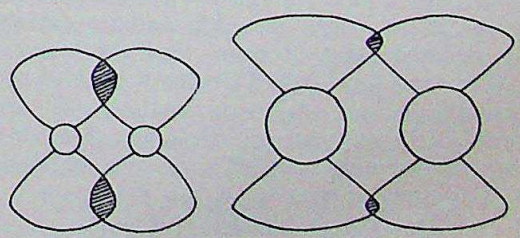


Figure 1. $P_\pi - P_\pi$ overlap between (right) two N atoms and (left) two P atoms (adapted from Pitzer (*14*)).

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Class 3.

Class 3 compounds are those whose instability is related to the reluctance of certain atoms of the first long period to assume their highest oxidation state.

A well-known consequence of this phenomenon is the fact that $AsCl_5$ has never been prepared, while its congeners in neighboring periods, viz., PCl_5 and $SbCl_5$, are familiar compounds (*16*). Further examples are shown in the following table, where the compounds in parentheses are either non-existent or of low stability:

PCl_5	SF_6	PCl_5	SO_3	$HClO_4$
(VCl_5)	(CrF_6)	($AsCl_5$)	(SeO_3)	($HBrO_4$)
$NbCl_5$	MoF_6	$SbCl_5$	TeO_3	HIO_4

The instability of the members of this class of compound can be traced (*17*, *18*) to the firmness with which the 4*s* electron pair is bound in atoms such as As, Se and Br. The build-up in nuclear charge which occurs across the first transition series, and the comparatively weak screening power of the 3*d* electrons, together have the effect of increasing the energy necessary to uncouple the 4*s* electrons. Uncoupling of the 4*s* electron pair is necessary if the atoms are to exert their highest valence state. A measure of this effect can be obtained by calculating from ionization potential data the difference between (*a*) the energy required to remove an electron from an s^2p ion (e.g., As^{2+}, Se^{3+}), in which the $4s^2$ pair remains intact, and (*b*) that required to remove an electron from an s^2 ion (As^{3+}, Se^{4+}), in which the $4s^2$ pair is uncoupled. These differences are plotted for the series S, Se, Te and P, As, Sb, in Figure 2. The much larger differences for Se and As are strikingly apparent. It is noteworthy that the highest oxidation state is sometimes achieved by the fluoride (e.g., in AsF_5 and SeF_6, but not in BrF_7); the reason for this is considered in the discussion of PH_5 in the final class.

Class 4.

Class 4 consists of compounds whose instability is related to the reluctance of certain atoms to undergo self-linkage (catenation).

The best known example in this category is the non-existence of compounds containing more than two singly-bound oxygen atoms. Thus there are no oxygen analogues of the S_8 molecule, or of the polysulfide ions S_3^{2-}, S_4^{2-}, S_5^{2-}, and S_6^{2-}, or of the polythionate anions $O_3S{\cdot}S_3{\cdot}SO_3^{2-}$ and $O_3S{\cdot}S_4{\cdot}SO_3^{2-}$. Still longer —S—S— chains are believed to be present in liquid sulfur, where the average chain length is about 1.5×10^6 Å at 171°C (*19*), and in some polythionates, where the chain may contain up to 80 sulfur atoms (*20*). The —O—O— chain length on the other hand is restricted to two atoms, as in hydrogen peroxide and its derivatives. In the isolated cases of ozone and the ozonide ion (O_3^-), there are three linked O atoms, but the bonding here is multiple; the curious molecule O_4 (*21*) appears to consist of two O_2 molecules held together by bonds that are much weaker than ordinary covalent bonds.

The instability of O—O single bonds is clearly related to the low O—O single bond energy compared to the much greater stability of the multiple bond in molecular O_2. It is well known that the N—N, O—O, and F—F single bond energies are unexpectedly low, as shown in Table 2. The "normal" pattern of variation within

Table 2. X-X Single-bond Energies, kcals/bond (22).

C-C	N-N	O-O	F-F
83.1	38.4	33.2	36.6
Si-Si	P-P	S-S	Cl-Cl
42.2	51.3	50.9	58.0
Ge-Ge	As-As	Se-Se	Br-Br
37.6	32.1	44.0	46.1
Sn-Sn	Sb-Sb	Te-Te	I-I
34.2	30.2	33	36.1

a group is exemplified by the sequence C—C, Si—Si, Ge—Ge, Sn—Sn, within which the bond energy decreases as the group is descended. This trend is associated with the general increase in diffuseness of the atomic orbitals as the atomic size increases, and a concomitant poorer overlap on homopolar covalent bond formation. For the smallest atoms in the groups 5, 6 and 7 sequences however, the N—N, O—O, and F—F values are all very low, an effect that is commonly attributed (*23*, *24*) to "lone-pair repulsion," that is, to repulsion between the non-bonding electron pairs present in the valence shells of the N, O, and F atoms in such single-bonded molecules as $H_2N—NH_2$, HO—OH, and F—F. (This view is not shared by Mulliken (*15*), who attributes the irregularities in the group 5, 6, and 7 sequences to a strengthening of the X—X bond in the second and subsequent rows by *d*-orbital hybridization, as has been discussed under class 3.) While the energy of the O—O single bond is low (33.2 kcals), that of the multiple bond in O_2 is considerably more than twice as large (118.3 kcals) and thus there is an inherent tendency for compounds containing O—O single bonds to decompose and form molecular O_2. No such tendency exists in the case of sulfur, however,

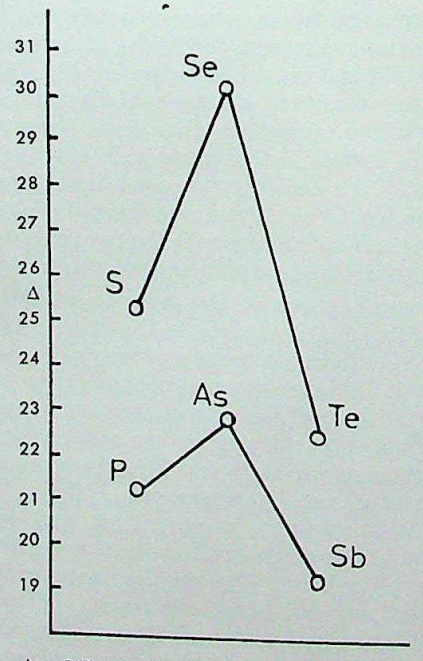


Figure 2. Δ = Difference between 4th and 5th (S, Se, Te) or 3rd and 4th (P, As, Sb) ionization potentials (ev.)

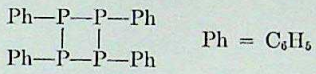
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because of the instability of the multiple bonds (discussed in class 3) and accordingly S—S single bonds are very common.

Much the same reasoning accounts for the paucity of compounds containing N—N single bonds. Although hydrazine ($H_2N \cdot NH_2$) and its derivatives are well known, and the very unstable compound tetrazane ($H_2N \cdot NH \cdot NH \cdot NH_2$) has been prepared (*25*), the high stability of the triple bond in molecular N_2 (bond energy = 226 kcals) suggests that the number of stable compounds containing N—N single bonds will always be severely limited.

In view of the widespread occurrence of S—S single bonds, the comparatively limited extent of P—P bonding in phosphorus compounds is surprising; the S—S and P—P bond energies are of comparable magnitudes (see Table 2). P—P bonding is observed in the P_4 molecule (white phosphorus), and in the red and black allotropes. In phosphorus compounds, two P atoms are directly linked in P_2H_4, P_2Cl_4, and P_2I_4 (P_2F_4 and P_2Br_4 seem never to have been made), and in the diphosphite ($HP_2O_5^{3-}$) and hypophosphate ($P_2O_6^{4-}$) ions; compounds in which three P atoms are linked are very few indeed, and include the sulfides P_4S_3 (*26*) and P_4S_5 (*27*), while four are presumably found in "phosphobenzene," $(C_6H_5)_4P_4$, to which Kuchen and Buchwald (*28*) have assigned the cyclic structure



Van Wazer (*29*) has suggested that certain lower hydrides of phosphorus—amorphous yellow solids of variable composition—may consist of three-dimensional networks of singly-linked phosphorus atoms containing terminal —PH_2 units and bridging —PH— and —P— units, and that it might be possible to obtain from such material molecular hydrides to continue the homologous series of which phosphine PH_3 and diphosphine P_2H_4 are the only known members.

Class 5

Class 5 consists of compounds whose instability is due to the "inert pair" effect.

It is known empirically that the elements following the transition series in each periodic row form compounds in which two of the valence electrons are not involved in bonding. The formation of such compounds (e.g., TlCl, $PbCl_2$, $BiCl_3$), in which the valence state of the element is two less than the group valence, becomes more apparent as each group is descended, and is most marked in the heaviest elements. This phenomenon has been described (*30, 31*) in terms of the existence of an "inert pair" of electrons in the *s* orbital of the valence shell. Thus the stable valence states of thallium, lead, and bismuth are I, II, and III, respectively, and in consequence, compounds exhibiting the group valence state are relatively unstable and easily reduced. In cases where the anion is easily oxidized, they have never been prepared. Examples are $TlBr_3$, $PbBr_4$, PbI_4, $BiCl_5$, $BiBr_5$, and BiI_5.

The causes underlying this effect have been examined by Drago (*32*), and it seems clear that the phenomenon cannot be attributed simply to a lack of reactivity associated with the *s* electron pair of the valence shell. A measure of the reactivity of the *s* electrons can be obtained in two ways, viz. (*a*) from ionization potential data, which give the energy necessary to completely remove the *s* electrons from the gaseous atom, and (*b*) from promotion energy data, which give the energy necessary to promote an *s* electron into a higher energy orbital. These energies are shown in Table 3 (*32*) for

Table 3. Energy Data

	2nd + 3rd ionization potentials (ev) $M^+(g) - 2e \rightarrow M^{3+}(g)$	promotion energy (ev) $M, s^2p(g) \rightarrow M, sp^2(g)$	$\Delta H°_{298}$ (kcals.) $M(g) + 1^1/_2\ Cl_2 (g) \rightarrow MCl_3(g)$
Ga	51.0	109.5	−172.4
In	46.9	100.8	−147.6
Tl	50.0	108	−109.4

the elements Ga, In, and Tl, which form a typical series. It can be seen that the trend in each case is irregular, and does not parallel the empirical fact that the "inert pair" effect becomes more pronounced as the group is descended. It is possible however to obtain from available thermodynamic data (*32*) a measure of the *covalent bond strength* in the trichlorides of these elements, *i.e.*, $\Delta H°$ for the reaction

$$M(g) + 1^1/_2Cl_2(g) \rightarrow MCl_3(g)$$

and the results are shown in the last column of Table 3. Clearly there is a substantial and regular decrease in the M—Cl bond strength as the series is descended and the bonding atomic orbitals become more diffuse, and the decrease in stability of the tervalent compounds is obviously a consequence of this. Unfortunately the thermodynamic data available are not sufficient to permit an extensive examination of the problem, but Drago is of the opinion that the heavier elements in each group cannot form sufficiently strong covalent bonds to supply the energy needed to promote the *s* electrons into bonding hybrid orbitals. Such elements therefore tend to form compounds in which the *s* electron pair remains intact.

Class 6.

Miscellaneous compounds are grouped in Class 6. PH_5 and related compounds.

In the group 5 sequence of elements N, P, As, Sb, Bi, the formation of 5-covalent compounds MX_5 is not observed where M = nitrogen (as discussed in class 1), and such compounds are often unstable where M = arsenic (as discussed in class 3), and where M = bismuth (and to some extent antimony), as discussed in class 5. Phosphorus, however, forms a familiar series of PX_5 compounds, including the three halides PF_5, PCl_5, and PBr_5, and even phosphorus pentaphenyl, $P(C_6H_5)_5$. It is therefore surprising that PH_5 has never been prepared. An indication of the reasons for this can be obtained by considering the energetics of the reaction

$$PX_3(g) + X_2(g) \rightarrow PX_5(g) \qquad (1)$$

and considering initially the specific cases of PCl_5, which does exist, and PH_5, which does not. The three

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steps contributing to the over-all reaction (1) are:

Step a: the (endothermic) promotion of a lone-pair electron of the phosphorus atom into a *d* orbital (or more correctly, into a hybrid orbital which has a proportion of *d* character).

Step b: the (endothermic) fission of the X-X covalent bond.

Step c: the (exothermic) combination of the excited PX_3 molecule with two X atoms to yield PX_5.

Although the enthalpy changes for all of these steps are not known precisely, it is clear that reaction (1) is much *less* likely to proceed for PH_5 than for PCl_5 for the following reasons:

1. It has been shown (*13*) that the $s \rightarrow d$ transition necessary to provide the hybrid orbitals involved in the formation of a PX_5 molecule is facilitated if X is highly electronegative; since the electronegativity of chlorine is considerably higher than that of hydrogen (e.g., on Pauling's (*33*) scale, Cl = 3.0 and H = 2.1), step *a* will be *less endothermic* for Cl than for H.

2. The heat of atomization (*34*) of Cl_2 (29.01 kcals/gram atom) is considerably less than that of H_2 (52.09 kcals/gram atom), so that step *b* will also be *less endothermic* for Cl than for H.

3. The heat of reaction for step *c* is of course unknown for PH_5, but bond energy values for the *tervalent* molecules are (*22*) P—H = 76.4 kcals and P—Cl = 79.1 kcals, which suggest that the P—H and P—Cl bonds may be of comparable strengths in the PX_5 molecules. If this is the case, then step *c* does not play a large part in determining the relative stabilities of PH_5 and PCl_5. The non-existence of PH_5 can therefore be traced largely to the effects of the high H—H bond energy and the relatively low electronegativity of the H atom.

Phosphorus (V) iodide, PI_5, has also never been prepared; the determining factor here may be the inadequate electronegativity of iodine, although the stereochemical difficulty of packing five large iodine atoms around the central phosphorus atom may also play a part.

Reasoning similar to the above can be developed to explain the non-existence of hexa-covalent derivatives of sulfur other than the hexafluoride—e.g., SH_6.

Participation of F in hydrogen bonding. Schomaker (*35*) has pointed out that in general fluorine atoms attached to carbon do not have significant power to act as proton acceptors in hydrogen bond formation. In view of the exceptional electronegativity of fluorine, and the high polarity of the C—F bond, it is surprising that substances containing hydrogen bonds such as $R_3C—F\cdots H—OR$ do not seem to have been prepared.

A number of compounds remain whose apparent non-existence the reader is invited to consider. These are (1) *dimeric* boron halides and alkyls (*cf.* Al_2Cl_6, dimeric aluminum trimethyl); (2) bromous and iodous acids (*cf.* $HClO_2$); (3) iodine monoxide (*cf.* F_2O, Cl_2O, Br_2O); (4) coordination compounds of molecular nitrogen, N_2 (*cf.* coordination compounds—carbonyls—formed by the iso-electronic molecule CO).

In some of these cases, and of others discussed in the previous classes, it may well be that the "missing" compounds will eventually be prepared, by appropriate choice of reaction path and reaction conditions. In others, it seems clear that thermodynamic circumstances will always preclude their formation. Whichever is the case, the search for an answer to the question "why has compound X never been prepared?" is unlikely to fail as a stimulating exercise for the student of chemistry.

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Electronic Spectra of Transition Metal Complexes

The colors and absorption spectra of complexes of the transition metal ions have intrigued chemists for a long time. It has been possible only recently to make quantitative predictions of the spectral properties of these molecules, as well as to find a theoretical rationale for much of the experimental data. This review will deal with some of the theoretical interpretations of the visible spectra of transition metal complexes, in an attempt to show some of the recent advances in this field as well as to point out some of the details omitted in most research papers. A knowledge of crystal field theory as explained by Sutton (*1*) shall be assumed. McClure (*2*), Dunn (*3*), and Ballhausen (*4*) have given more complete reviews of the literature in this field.

The basic phenomenon to be considered is the resolution of the degeneracies of eigenstates of the free metal ion by the imposed crystalline field. Once we understand which energy levels are available in a complex, it follows that the absorption spectrum will arise from electronic transitions from the ground state to the various excited states. Due to the selection rules of quantum mechanics, some of these transitions are not allowed while others are allowed only under certain conditions.

The Spectrum of Ti^{3+}

In order to define terms and introduce the basic ideas to be used, it is appropriate to begin with a discussion of the spectrum of trivalent titanium. This ion is not only typical in that it forms octahedral complexes with many ligands; but it is the simplest that can be considered, since we shall have to deal with but one d electron outside the argon shell. The ground state is thus ^2D. The free ion upon being placed in a crystal undergoes a spherically symmetrical repulsion V_R which causes a shift of the ground state but does not split the fivefold degeneracy. An additional potential arising from the symmetry of the cationic site will split this level. The ^2D term of Ti^{3+} is split by an octahedral field, V_{Oh}, into two levels, the lower, triply degenerate $^2T_{2g}$, and the higher, doubly degenerate ^2E_g. The energy separation between these levels is defined as 10 Dq, and is some 20,300 cm^{-1} for the hexaquotitanium (III) ion. See Figure 1. The energy separation between $^2T_{2g}$ and ^2E_g must preserve the center of gravity of the ^2D level. That is, the triply-degenerate set of levels is lowered in energy by 4 Dq and the doubly-degenerate set is raised by 6 Dq.

Now we have an idea of the order of magnitude of the electronic splittings in complex compounds. The spectrum of $Ti(H_2O)_6^{3+}$ has yielded a value for Dq of 2030 cm^{-1}. It is important to notice the very small energies involved in such crystal field splittings. A perturbation of electronic levels of 20,000 cm^{-1} in a complex is small compared to the total binding energy of such a compound.

If one were now to replace the water molecules in the coordination sphere of the titanium (III) ion by chloride ion, one might expect a small change in the observed spectrum. Although this particular experiment does not seem to have been completed yet, we know from a comparison with similar systems containing other metal ions that the absorption peak would shift to lower energies. In other words, Dq is smaller for Cl^- than for H_2O as ligands. By studying all available ligands against one central metal ion, a spectrochemical series is found which places the ligands in order of increasing field strength. Such a series is: $I^- < Br^- < Cl^- < OH^- < F^- < H_2O <$ oxalate $<$ pyridine $< NH_3 <$ en $< NO_2^- < CN^-$.

Energy-level diagrams similar to that above may be drawn for all the transition metal ions, having from one to nine d electrons. (In this connection, it is worth while to remember the reciprocity of d^n and d^{10-n} systems.) The polyelectronic atoms have more atomic terms present, so that more energy levels are usually found, causing a richer spectrum. States of different spin multiplicity may also enter as will be discussed below.

It is well to note at this time that the labeling of levels as T_{2g} and E_g holds only for purely octahedral fields. Such a symmetry about a metal ion rarely occurs in the crystal, and vibrations of the ligands tend to distort the field in solution. The effect of this distortion on the spectrum is in direct relation to the magnitude of the distortion. For example, the absorption curve of the aquated Ti^{3+} ion is somewhat asymmetric, which has led some authors to suggest that the symmetry of the hydrated ion is less than octahedral.

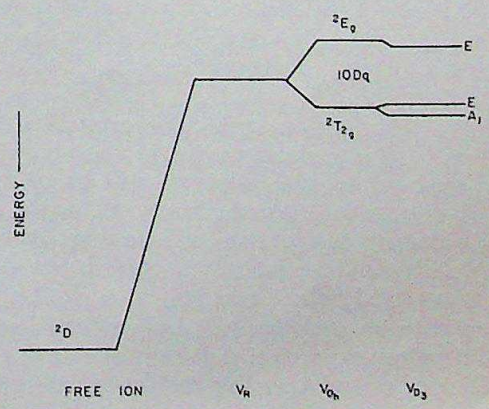


Figure 1. Energy level diagram for d^1 in octahedral and trigonal field.

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(The asymmetric distortion will partially break-up the degeneracy of the ^2E_g level; transitions to two near-by levels will cause an asymmetric broadening of the absorption band.) As we shall see, the intensities of absorption bands depend on the presence of an asymmetric field.

A field of lower symmetry will tend to further resolve the degeneracies found in an octahedral field. Consider the compression or elongation of the coordination octahedron along a three-fold axis passing through opposite faces of the octahedron. This trigonal distortion lowers the cubic symmetry about the metal ion and requires the breaking up of all triple orbital degeneracies. Thus $^2E_g \rightarrow {}^2E$, $^2T_{2g} \rightarrow {}^2A_1 + {}^2E$, where now A_1 is a label referring to a singly degenerate (orbital) level. If the A_1 state should be the ground state, and if the splitting of $^2T_{2g}$ is sufficiently large, we should then expect to see electronic transitions from the ground state to each of the ^2E levels. This has not yet been observed for trivalent titanium.

Energy Level Diagrams

All the information necessary to interpret the spectra of transition-metal complexes (neglecting spin-orbit coupling) is included in the energy level diagrams of Orgel (*5*) and Tanabe and Sugano (*6*). It will be of value to include in this review a discussion of these diagrams and their use, as well as some of the matrices used to derive the diagrams. We shall discuss each scheme, classifying them for convenience only as weak field (Orgel) and strong field (Tanabe and Sugano).

Weak Field

The matrices of Orgel (*5*) and the resulting diagrams are based on the weak field model of a complex: one considers the free ion wave functions and then seeks the result of imposing a crystal field on the central ion. In other words, one determines the terms of the free ion and then "turns on" the crystalline field and looks for the resulting changes in energy levels.

Let us consider Mn^{2+}:$3d^5$. In the weak-field scheme, there are five unpaired electrons, so the multiplicity of the ground state is $2(5/2) + 1 = 6$. The ground state has no orbital (or spacial) degeneracy so its symbol is ^6S, or, to use the symmetry designation, $^6A_1$. All low-excited states will keep the electrons within the $3d$ manifold, so there must be a change in spin-multiplicity upon absorption (e.g., in the one-electron orbital designations, $t_{2g}^3e_g^2 \rightarrow t_{2g}^3e_g^2$, where the only change involves a flipping of one of the electron spins) and all the excited states will be quartets. For the first few states, the terms (and orbital degeneracies) are $^4G(9)$, $^4P(3)$, $^4D(5)$, and $^4F(7)$.

Now the perturbation by a cubic crystalline field is turned on. All the degeneracies in the above states will be removed so that no level will be more than threefold degenerate. Furthermore, all levels of the same symmetry designation will interact with one another. We shall be interested only in the energies of the respective levels.

These energies are obtained by writing down the potential energy expression that corresponds to a cubic crystalline field and then by first-order perturbation theory calculating the interaction of this potential with each of the atomic terms. That is, the new energies of the perturbation, expressed in terms of Dq, are obtained as the so-called matrix elements,

$$H_{ij} = \int \psi_i V_{oh} \psi_j d\tau$$

Remember that for one electron,

$$\int t_{2g} V_{oh} t_{2g} d\tau = -4Dq$$

The non-diagonal terms are those for which $i \neq j$, or those terms where one energy level interacts with another because of the octahedral potential. A separate matrix is set up for each set of terms of the same symmetry.

For example, the resulting matrices for Mn^{2+} in either octahedral or tetrahedral field are:

$^4T_1$	^4P	^4F	^4G
^4P	0	0	$4\sqrt{5}\ Dq$
^4F	0	0	$2\sqrt{5}\ Dq$
^4G	$4\sqrt{5}\ Dq$	$2\sqrt{5}\ Dq$	0

$^4T_2$	^4D	^4F	^4G
^4D	0	$(20/\sqrt{7})\ Dq$	0
^4F	$(20/\sqrt{7})\ Dq$	0	$\frac{10\sqrt{3}}{7}\ Dq$
^4G	0	$\frac{10\sqrt{3}}{7}\ Dq$	0

^4E	^4D	^4G
^4D	0	0
^4G	0	0

Before going further it must be pointed out that these matrices refer only to the cubic perturbation on the metal ion; in order to obtain the *complete* energy level scheme, one must also include the energy of each free ion term with respect to the ground state. This is done by placing the values of these energies for each term along the matrix diagonals.

Before considering the diagram resulting from the use of these matrices, one can learn something about the energy level scheme by examining the matrices. The resolution of free-ion degeneracies is readily apparent: thus, ^4G yields $^4E + {}^4T_1 + {}^4T_2$ states in a cubic field. Note also that all diagonal elements are zero. The ^4E states (one each from ^4D and ^4G) do not perturb each other at all; their energies in a complex should be the same as that in the free ion. This fact has often been used in comparing the position of atomic terms to the corresponding term in the complex.

The energy level diagram is obtained by substituting a series of values for Dq and plotting the calculated energy of each level as a function of Dq. The resulting energy level diagram for Mn^{2+} is shown in Figure 2; an analogous diagram applies to isoelectronic Fe^{3+}, but with a different positioning of the free-ion states. The zero of energy is the ground state, $^6A_1$.

Orgel (*7*) has used this diagram to assign the spectrum of the manganese (II) ion. He found that all of the atomic terms of Mn^{2+} were lowered in the complex relative to the free ion. Thus, $^4E_g(^4G)$ was found to be about 1800 cm^{-1} below the position in the free ion. Similar corrections of 2600 and 2200 cm^{-1} were applied, respectively, to the ^4D and ^4P levels. This lowering of term values apparently means that the electron-electron repulsions are lower in the complex than in the free ion. This has been cited as evidence for covalence in complexes, as interactions of the metal d

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electrons with the ligands would decrease the electron-electron repulsions. There is no obvious quantitative correlation, however, between term lowering and per cent covalency.

Note that all transitions from the ground state for the Mn^{2+} and Fe^{3+} ions involve a change in spin-multiplicity—it is apparent (*cf.* below) that all observed transitions will be of very low intensity for either of these ions. The related question of the breadth of the spectral bands of manganese (II) ion has also been discussed by Orgel (*7*). He points out that the greater the slope of a line in the above diagram, the broader will be the observed spectral transition. This is due to a change in the distribution of electrons (between the ground and excited states) that changes the number of t_{2g} and e_g electrons. This in turn affects the radius of the metal ion and the corresponding equilibrium configuration. As the system approaches the equilibrium configuration of the excited states, a number of vibrational transitions are excited, thereby causing a broad band. Transitions to ^4E_g, $^4A_{1g}$ (G) are noted for their sharpness, on the other hand. Orgel (*5*) has published the analogous matrices and diagrams for the remaining d^n systems.

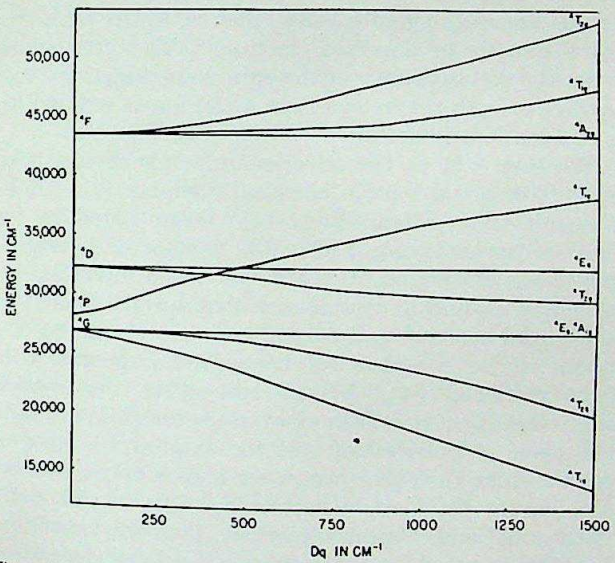


Figure 2. Energy level diagram for d^5 (Orgel (*5*)).

Strong Field

It will now be worthwhile to discuss the energy level diagrams of Tanabe and Sugano (*6*). The scheme used is the strong-field one, which places the electrons in the t_{2g} and e_g orbitals (one-electron orbitals) and then measures the interaction. Here, one considers the crystal field to be stronger than the electron-electron repulsions, and obtains no information from the free ion term values. Rather, one must independently evaluate Racah's B and C, the parameters of electrostatic interaction. (These are $B = F_2 - 5F_4$ and $C = 35F_4$, where the F_i are the familiar Slater-Condon-Shortley parameters.) In the limit of intermediate fields these diagrams must correspond to those of Orgel.

We shall later discuss some spectra of Cr^{3+}, so it will be useful to present the appropriate diagram for $3d^3$:Cr^{3+} in Figure 3. The ordinate is energy in units of B and the abscissa is Dq/B. The parameter B (and C, as well) arises from the e^2/r_{12} term in the Hamiltonian for the system; it is simply a measure of the electron-electron repulsion. The ground state of the metal ion is always the abscissa line in the diagrams.

On the diagram for Cr^{3+}, we find both the quartet and doublet states. Values of B and C were estimated by extrapolating from known term values. We do not present the Tanabe-Sugano matrices here as they are somewhat more complicated than Orgel's for most ions, but refer the interested reader to the original papers (*6*) or McClure's review (*3*).

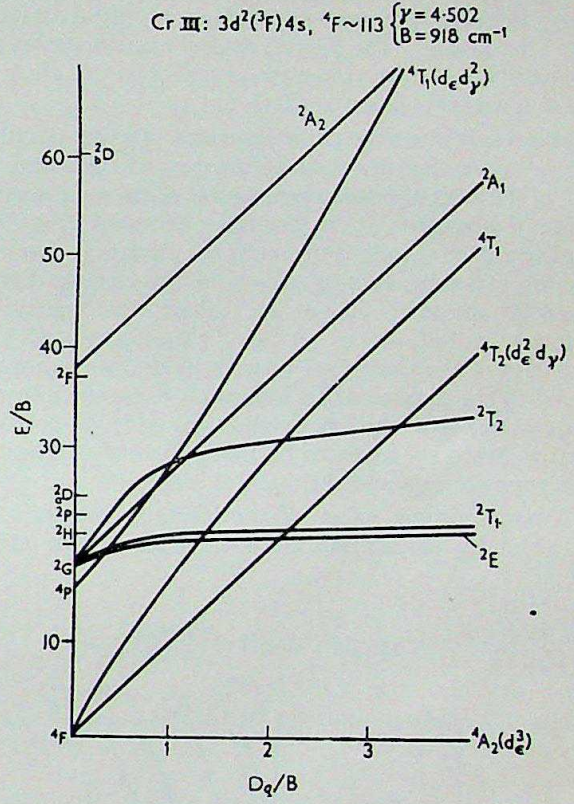


Figure 3. Energy level diagram for d^3 (Tanabe and Sugano (*6*)).

For systems with more than three electrons, a change in ground state (weak field → strong field) can occur at a critical value of Dq/B; this is indicated by a vertical line on the diagram where the change occurs. This is illustrated by the following diagram for Co^{3+}:$3d^6$. Most chemical compounds of cobalt(III) ion are diamagnetic, indicating the $^1A_1$ (spin-paired) ground state occurs.

The diagrams of Orgel and Tanabe and Sugano are not perfect. The most serious problem is that the term values found in a complex are generally lower than those of the free ion yet neither diagrammatic scheme accounts for this. Further they are simply the best fit that can be made with the available data; the diagrams thus refer to the general properties of a metal ion rather than to a specific complex. Although the diagrams refer only to octahedral coordination of the metal ions, they are readily extended to include the effects of fields of lower symmetry.

Selection Rules and Intensities

The number and kind of energy levels which are

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available in a particular complex have been discussed, so now we need to learn whether a transition from the ground state to one or more of these does indeed occur—i.e., is a particular transition allowed or forbidden by the selection rules. Selection rules are a quantum-mechanical phenomenon, arising from the various properties of the wave functions representing each of the eigenstates.

Consider first the free gaseous metal ion. The type of transition we have been looking at is forbidden by the rules of quantum mechanics for it occurs between two levels arising from the same term of the atom. In other words, crystal field spectra are $d \rightarrow d$ transitions: the electronic process involves only the d orbitals of the metal ion. The d levels are even under inversion and an even → even transition is forbidden for electric dipole radiation (Laporte's Rule).

This result is conveniently expressed mathematically. Let ψ_1 be the eigenfunction of the ground state and ψ_2 that of the excited state, where ψ_1 and ψ_2 are some appropriate d orbitals. It is generally accepted that the electric vector of radiation causes the electronic spectra, and we represent this by means of the electric dipole moment operator, $\mu_E = -ex$. Then the transition moment is defined as $P_E = \int \psi_1 \mu_E \psi_2 d\tau$, and the intensity of the transition between ψ_1 and ψ_2 is proportional to the square of this integral. Since the integral is over two even functions and one odd, all positive contributions are canceled by those of equal magnitude and opposite sign and the integral is zero.

A nonvanishing value for the intensity may still be obtained by considering the interaction of the atom with the magnetic dipole vector of light. Thus consider the integral

$$P_M = \int \psi_1 \mu_M \psi_2 d\tau$$

where now

$$\mu_M = \frac{-e}{2mc} M_x$$

and M_x is the angular momentum operator

$$\frac{\hbar}{i}\left[y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right]$$

The operator μ_M is an even one (M_x does not change sign under inversion, $(x, y, z) \rightarrow (-x, -y, -z)$), and so P_M is non-zero and the d-d transition is allowed in the free gaseous ion by a magnetic dipole process. Note that we have only shown that P_M need not be zero on symmetry grounds; the actual value of P_M may still work out to be small or even zero. A probably less important process which we shall not mention further is that caused by electric quadrupole radiation.

As yet only the orbital selection rules for a free gaseous metal ion have been discussed. For polyelectronic ions, the question of spin selection rules enters. We find that transitions are allowed only between levels of the same spin multiplicity, that is, levels with the same number of unpaired electrons. This rule arises from the orthogonality of the spin wave functions and applies to both the free gaseous metal ion as well as the metal ion in a complex.

We turn now to the selection rules for crystal field spectra of metal ions in chemical compounds. All of the spin-allowed transitions have been found to be electric dipolar in origin (*2*). The method of determining this is illustrated by Figure 5. Let a metal ion be placed in a uniaxial crystal such that spectra along the axis (axial spectra) and normal to it (σ, π) can be obtained. The σ and π spectra refer to spectra with light polarized ($\perp$, $\parallel$) with respect to the crystal axis; the direction of the electric vector E determines the plane of polarization If the axial and σ spectra are the same then the spectra are shown to be electric dipolar, for the electric vectors coincide in this case. If the axial and π spectra coincide, then the transition has been induced by the magnetic dipole of the radiation.

Since we are still dealing with d-d transitions we must ask how the selection rules for the free ion have been changed in order to allow the electric dipole mechanism. If the character of ψ_1 and ψ_2 could be

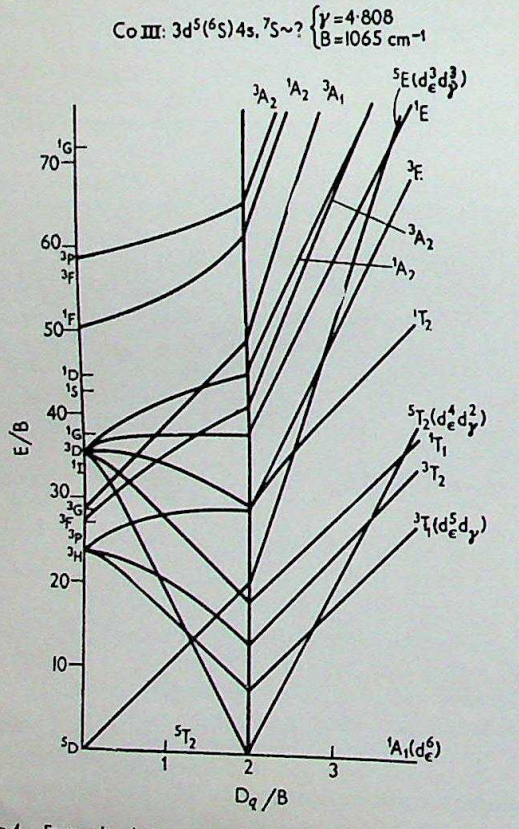


Figure 4. Energy level diagram for d^6 (Tanabe and Sugano (*6*)).

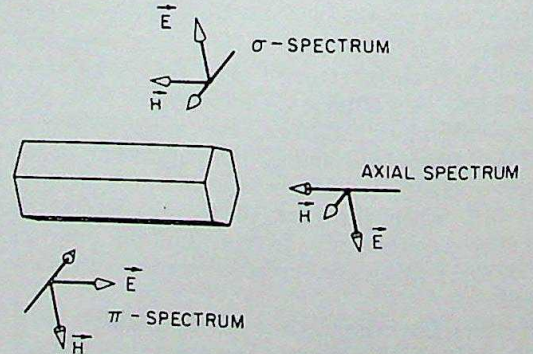


Figure 5. Polarized spectra of a uniaxial crystal (McClure (*2*)).

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changed such that they were no longer pure d functions, but rather were mixed with some p (odd) character then P_E might no longer be zero. Thus, we would like the ψ_i to become

$$\psi_i' = \psi(3d)_i + \alpha\phi(4p)_i$$

where α is a mixing coefficient. The odd nature of the $4p$ functions, combined with the odd μ_E, will allow P_E to be nonvanishing.

Physically, in order to mix the $3d$ and $4p$ functions, we need to remove the inversion center (symmetry element i) about the metal ion. Two obvious mechanisms for removing i are to allow odd vibrations of the surrounding ligands, or else to place the metal in a statically distorted field.

In a strictly cubic crystalline field, the vibrations of the complex are certainly the mechanism of interest. In those cases where octahedral coordination of the metal ion has been found, the source of intensity has always been ascribed to the vibrations. Ballhausen (*8*) has reviewed the intensities of spectral bands with particular emphasis on the vibronic (vibrational interaction with an electronic process) mechanism.

Spin-forbidden transitions, which appear as very weak lines in the spectra of several transition metals, have been found to be magnetic dipolar in the case of cubic MgO : Cr^{3+} (*9*). This distinction from the vibronic mechanism was made by means of Zeeman studies.

The case where the asymmetric field is caused by a static perturbation has received much less attention, both experimentally and theoretically, although there is ample evidence of its importance. Several recent studies have shown that this mechanism can be more important than the vibronic mechanism in certain cases.

We mention first the case of tetrahedral complexes. There is no inversion center present in a tetrahedral complex, so Laporte's rule does not hold. One would then expect electronic transitions to be more strongly allowed causing a marked increase in intensity of the crystal field bands. Such is indeed the case. Gill and Nyholm (*10*) report the spectra of several compounds of formula $MX_4^=$ (M = Ni, Co, Cu, Mn; X = Cl, Br, I). Absorption bands in the visible (except for Mn; cf. above) have extinction coefficients in the range 200–1200, which are some 100 times greater than those for the octahedral hexaquo ions.

The effect of the absence of centrosymmetric fields on the intensity has been well illustrated by studies (*11*) on the spectra of *cis*- and *trans*- $[Co\ en_2X_2]^+$ (X = F, Cl) in aqueous solution. The *trans* isomer is, of course, centrosymmetric, while the *cis* compound lacks a center of inversion. The intensities as measured by the relative extinction coefficients are some 3 to 4 times more intense for the *cis* compounds.

The most convincing evidence for the importance of asymmetric fields for octahedral complexes in determining the intensities of spectra is provided in the recent study (*12*) of metal ions substituted isomorphously for part of the aluminum in the crystal $NaMgAl(C_2O_4)_3 \cdot 9H_2O$. This crystal is uniaxial, so the electric and magnetic dipolar effects were studied as shown in Figure 5. The metal ions are in a predominantly cubic field with a small trigonal distortion; the trigonal axis, furthermore, is aligned with the c axis of the crystal. The symmetry is high enough to afford the selection rules:

$$A_{1,2} \overset{\perp}{\leftrightarrow} E,\ A_{1,2} \overset{\perp}{\nleftrightarrow} A_{1,2} \text{ and } A_1 \overset{\parallel}{\leftrightarrow} A_2$$

The $\parallel, \perp$ refer to the polarization of the incident light beam with respect to the trigonal axis, while $\leftrightarrow\!\!|\!\!\rightarrow$ denotes a forbidden transition.

The selection rules were found to be well-obeyed in the cases of V^{3+}, Cr^{3+}, and Co^{3+}. For example, in the case of $NaMgCr(C_2O_4)_3 \cdot 9H_2O$, the second excited state is $^4T_{1g}$, which, under a trigonal distortion, goes to $^4A_2 + {}^4E$. The ground state is $^4A_2$. Thus $^4A_2 \rightarrow {}^4E$ is allowed and was found at 23,670 cm^{-1} in perpendicular polarization, with $\epsilon_\perp = 61$. However, $^4A_2 \rightarrow {}^4A_2(^4T_{1g})$ is not allowed, and the observed band is very weak and diffuse (Figure 6), and the ratio of extinction coefficients $\epsilon_\parallel / \epsilon_\perp$ is 0.06. Since the electronic selection rules based on symmetry alone apply so well, it was concluded that vibronic coupling was not important in determining the intensities.

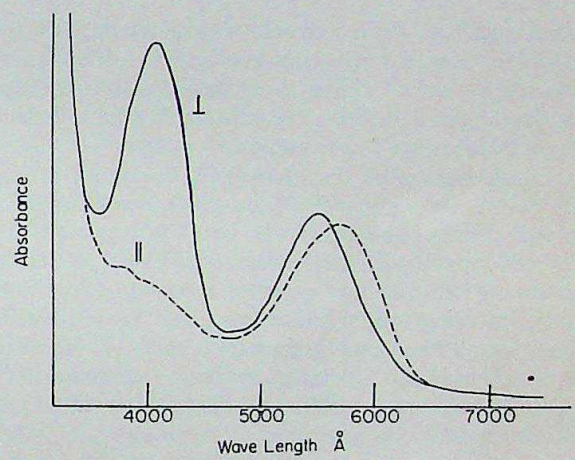


Figure 6. Polarized spectrum of $NaMgCr(C_2O_4)_3 \cdot 9H_2O$ (Piper and Carlin (*12*)).

The spectra were observed in both parallel and perpendicular polarization in this crystal, as well as along the axis. In all cases, the perpendicular spectra were found to coincide with the axial spectra showing the nature of these bands to be electric dipolar. Many of the spin-forbidden bands were observed as well. The absence of a center of inversion again allows these transitions to be electric dipolar in origin. By comparison of the perpendicular and axial spectra, it was found that all the spin-forbidden transitions were caused by the electric dipole vector of light.

In summary, we have seen how the intensity of spectral bands of transition metal complexes arises, and the nature of the selection rules governing the spectra. The importance of the symmetry of the field about the metal ion has been demonstrated as well.

Charge Transfer Spectra

A complete discussion of charge transfer spectra has been given elsewhere (*2, 4*). The very intense bands arising from charge transfer usually occur in the ultraviolet and are ascribed to the highly energetic transfer of electrons from either the donor atom to the

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central metal ion or vice versa. These bands are therefore Laporte allowed. In this section we wish to point out two cases where these bands interfere with the usual *d-d* bands, as well as to show how for several compounds a study of the charge transfer spectra has helped to unravel the molecular orbitals and *d-d* assignments in a complex.

We have already seen that electronic transitions of the iron(III) ion involve a change in spin-multiplicity and are therefore expected to be very weak in intensity. Examples of compounds where this rule holds are FeF_6^{3-} and $Fe(NO_3)_3 \cdot 9H_2O$. Yet the common qualitative test for iron(III) ion involves the deep red color caused by the interaction of thiocyanate with the ion, and iron(III) acetylacetonate is also found to be a deep red material. A careful examination of the spectra readily explains these unusually intense colors.

The first quartet excited states of iron(III) acetylacetonate occur at 9760 and 13,160 cm^{-1}, with respective extinction coefficients of 0.45 and 0.70 (*13*). These spin-forbidden bands have the expected low intensities.

The next transitions observed are at 21,230 and 28,410 cm^{-1} with extinction coefficients of 3250 and 3420, respectively. Since these bands arise, presumably, from spin-forbidden transitions, the large extinction coefficients are most unusual.

A consideration of the ultraviolet spectrum of iron (III) acetylacetonate will offer a ready explanation of these disparate intensities. A band is reported (*14*) at 36,600 cm^{-1} with extinction coefficient of 27,000. This strong band simply overlaps those close-by in the visible, altering their character and their relative intensities. The near infrared bands of iron(III) acetylacetonate are too far away from the energy level to be masked appreciably and thus show their true (spin forbidden) character.

A similar situation was found with the compound $[Mn(C_5H_5NO)_6](ClO_4)_2$ (*15*). This bright yellow compound stands in marked contrast to most manganese (II) compounds which are light pink. No *d-d* transitions were found in the visible spectrum but, rather, the charge transfer band was found at about 3800 Å. This intense band, occurring unusually close to the visible region, simply trails off into the visible, causing the yellow color. Such a phenomenon is also common with highly unsaturated organic molecules. These remarks show that there are certain pitfalls one must avoid in interpreting electronic spectra.

Ballhausen and Gray (*16–18*) have recently shown how one can apply molecular orbital theory to the charge transfer spectra of complexes. Their work involved calculation of the relative energies of both metal ion and ligand orbitals and consequent derivation of the suitable molecular orbital scheme. This scheme is then tested against the experimental spectra, making full use of *both d-d* and charge transfer spectra. The guiding principle in their assignments (and consequent verification of the M.O. schemes) has been that both a band's energy *and* intensity must be correctly accounted for.

The first ion treated in this way (*16*) was the vanadium(IV) ion, VO^{2+}. The electronic structure of complexes involving this ion, such as $VO(H_2O)_5^{2+}$, is completely dominated by the short vanadium-oxygen π-bond and the attendant strong tetragonal distortion. Molecular orbitals were set up to allow this strong π-interaction, with the other ligands (H_2O) acting predominantly as σ donors. The resulting scheme is shown in Figure 7. There is one *d* electron in the system, in the b_2 orbital, so the ground state of the ion-molecule is $^2B_2$. The crystal field transitions involve, respectively, promotion of the electron to the e_π^*, b_1^*, and then Ia_1^* orbitals, all of which are essentially metal ion orbitals; the corresponding energy levels are labeled $^2E(I)$, $^2B_1$, and $^2A_1$. The first two transitions are indeed observed, the first being more intense because it is orbitally allowed. Polarized spectra confirmed these assignments. The third transition is observed in a few vanadyl complexes as a shoulder on the first charge transfer band. The change in spectrum with solvent is also consistent with the M.O. scheme (*19*).

The low energy, charge transfer bands are due to promotion of an electron from the oxygen π orbital (e_π^b) to the metal ion b_2 and e_π^* orbitals. In this transition an electron is moved from a delocalized π orbital into an occupied b_2 orbital localized on the vanadium atom, and the considerable repulsion energy associated with this process was estimated in the prediction of the spectrum. Excellent agreement was obtained between calculated and experimental band energies and intensities.

Similar studies have since been carried out on some nitrosyls (*17*) and square-planar diamagnetic d^8 complexes (*18*). These papers by Gray and Ballhausen are strongly recommended to those looking for an introduction to the use of molecular orbital theory in predicting the spectral (and magnetic) properties of complex ions.

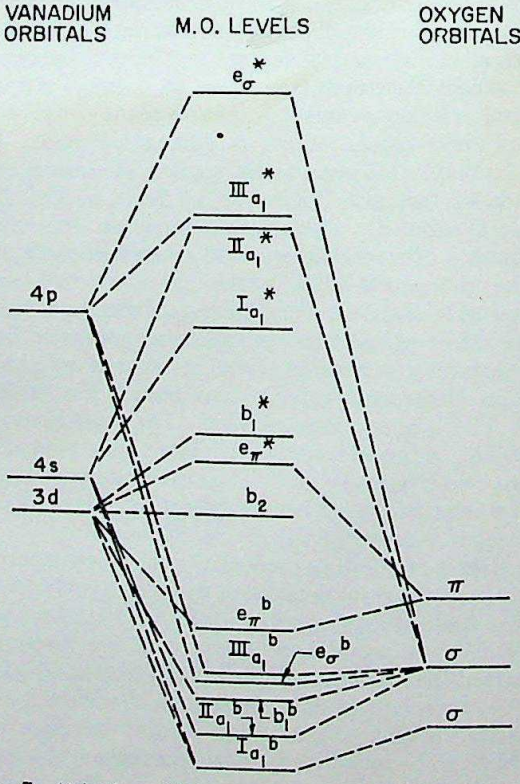


Figure 7. Molecular orbital scheme for vanadyl ion (Ballhausen and Gray (*16*)).

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Spectra: Several Examples

Now that the selection rules and energy level diagrams governing the spectra of transition metal complexes have been presented, we can go on to discuss several spectra and their interpretation. Despite the recent interest in crystal field theory, it is surprising to find how few systems have been worked out in complete detail. An excellent example is the work of Heidt, Koster, and Johnson (*20*) who studied the spectrum of the aqueous manganous ion. A perchloric acid medium was used in order to minimize hydrolysis. Measurements were made between 9 and 55°C but no significant change in the spectrum with temperature was noticed.

The spectrum was scanned between 8000–2000 Å or 12,500–50,000 cm^{-1}. A number of maxima, minima, and shoulders were observed, although only the maxima below 30,000 cm^{-1} were readily assigned. Extinction coefficients for the band maxima are characteristically of the order of 0.02; this is in accord with the fact that all the observed transitions are spin-forbidden.

The purpose of the work was to give a complete analysis and assignment of the spectrum in terms of the three parameters B, C, and Dq. There are a large number of peaks in the spectrum and a correspondingly large number of energy levels. Therefore, by using the Tanabe-Sugano matrices for d^5, the parameters were fitted to the spectrum simultaneously in order to obtain the best values. No attempt was made to interpret the resulting values of B, C, and Dq in terms of a fundamental theory; there is no quantitative explanation for the values of these parameters nor is there a fundamental way of predicting their variation. The best values (*19*) found for the parameters are:

	$B(cm^{-1})$	$C(cm^{-1})$	$10\ Dq(cm^{-1})$
$Mn^{2+}(g)$	786	3790	0
Mn^{2+} (aq)	671	3710	8480

Note the relatively small changes in B and C upon going from the gaseous system to the hexaquo ion. Orgel, in his earlier interpretation of the spectrum of Mn^{2+}·aq, found it necessary to lower each term by a different amount. Such was not the case here, where one choice of parameters fit the experimental values (see Table 1).

Table 1. Calculated and Observed Spectrum

State	Calc. (cm^{-1})	Obs. (cm^{-1})
$^4T_1(^4G)$	19,400	18,870
$^4T_2(^4G)$	22,800	23,120
$^4E, ^4A_1(^4G)$	25,200	24,960 25,275
$^4T_2(^4D)$	28,200	27,980
$^4E(^4D)$	29,900	29,750

It will be noticed that the degeneracy of ^4E, $^4A_1(^4G)$ has been partially removed. The degeneracy predicted for these levels is purely accidental and is due essentially to the approximations in the theory. A general interaction of cubic symmetry could remove this degeneracy.

The spectra of single crystals of MnF_2 have been studied at both room temperature and 20°K by Stout (*21*). The crystal contains Mn^{2+} surrounded by an octahedron of fluoride ions with a small orthorhombic distortion. Figure 8 shows the axial spectrum at room temperature. The general features of the bands (or lines) are quite similar to those of the aqueous manganese (II) ion. As with the oxalate crystal mentioned above, the axial and $\sigma(\perp)$ spectra were found to coincide, showing that the optical transitions are electric dipolar.

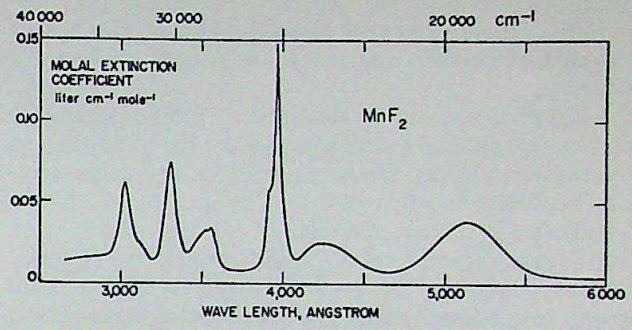


Figure 8. Spectrum of MnF_2 (Stout (*21*)).

Stout preferred not to use the Tanabe-Sugano matrices, for they do not take account of the change in term values on going to a complex ion. Rather, he recast the matrices in terms of a covalency parameter, ϵ which reduces the amplitude of each e_g orbital by the factor $(1 - \epsilon)^{1/2}$. This scheme then tries to account for the screening of the e_g electrons by their interaction with the fluoride ions. One needs now consider only ϵ and Dq as adjustable parameters, for the scheme uses the free-atom energy levels. The spectra were fitted well by a choice of $\epsilon = 0.064$ and $Dq = 780\ cm^{-1}$, which implies that the electrostatic interaction energy in the t_{2g} orbitals may be neglected.

A particularly fascinating application of the electronic spectra of complexes concerns their use as probes in studying the composition of ionic melts. For example, Gruen and McBeth (*22*) studied the absorption spectra of *four* oxidation states of vanadium in LiCl - KCl eutectic between 400 and 1000°C. The spectrum of V(II) consisted, at 400°, of three bands, with a total oscillator strength (integrated intensity) of 4.3×10^{-4}. The spectrum is fit by $Dq = 700\ cm^{-1}$, assuming octahedral stereochemistry. This value is only 60–65% as large as in water surroundings; the intensity of the spectrum, however, is about a factor of 10 greater than for aqueous solution. Orbital overlap between the ligands and the metal ion may account for this. The spectrum of V(II) in this melt is strongly temperature dependent, and the spectrum at high temperatures (1000°) indicates the formation of a tetrahedral $VCl_4^=$ species. It is obvious how this type of experiment will provide information on the structure of such ionic melts.

The spectrum of V(III) in LiCl-KCl eutectic at 400° can be fitted to an energy level diagram for a d^2 ion in octahedral symmetry with $Dq = 1200\ cm^{-1}$. Again, the value of Dq in the octahedral chloride environment is about 65% of the Dq of octahedral oxygen surroundings. High temperatures appear to induce the formation of tetrahedral VCl_4^-.

The spectrum of V(IV) in the eutectic was obtained on dissolved vanadyl ion. The spectra are similar to those mentioned earlier for vanadyl, consisting of a

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peak (13,530 cm^{-1}) and a weaker shoulder at higher energy (15,400 cm^{-1}). The V(IV) spectrum is quite temperature insensitive, the peak positions and band intensities remaining essentially unaltered in the range 400–1000°. This again indicates the fact that the V-O bond largely determines the spectrum, and that any change with temperature in the number of coordinating chloride ions has only a small effect on the spectrum.

The V(V) spectrum is characteristic of the charge transfer processes expected in a system with no *d* electrons.

Finally, the study of the spectra (and magnetism) of some tetrahedral complexes (*23–26*) has yielded some interesting auxiliary results as well as a definitive selection of electronic parameters. The spectra (*23*) of the tetrahedral tetrahalo manganese (II) complexes were fairly readily interpreted to yield values of Dq, B and C in the complexes. As mentioned above, the spectral bands are characterized by large intensities, being perhaps 100 times more intense than in octahedral complexes. The band intensities in the iodide are 5 to 10 times as intense as for the chloride or bromide. This may be an example of spin-orbit coupling acting at a distance. (The spin-orbit coupling parameter varies as the fourth power of the atomic number, so it is much larger for the iodide ion than for the other halides. The transitions in the $MnX_4^{=}$ spectra are all spin forbidden and are made partially allowed by spin-orbit coupling with excited states of the metal ion. This effect may be enhanced by increased spin-orbit interaction with the ligand.)

Studies on tetrahedral tetrahalo cobalt(II) (*24*) and nickel(II) (*25*) yielded similar results. An important part of this work was the comparison of the spectra of the complexes while in the solid state and in solution. Assuming that the solid state spectrum was the true spectrum of the $MX_4^{=}$ ion, some changes were observed on measuring the solutions, indicating solvolysis. It was further concluded that even in the most concentrated aqueous hydrohalic acids and lithium halide solutions complete conversion of Co(II) to CoX_4^{2-} species probably does not occur.

The work also yielded a good independent order of ligands not previously placed in the spectrochemical series; this order is

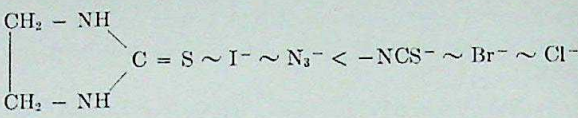
$$I^- < Br^- < -SCN^- < Cl^- \ll (C_6H_5)_3PO < N_3^- < -NCO^- \sim OH^- \ll -NCS^-.$$

The postulate of the average ligand field was also tested experimentally and verified. This postulate states that for a complex CoX_2Y_2, where X and Y are several ligands which do not differ sufficiently to produce distinct splittings of the spectral bands, it will be possible to treat this complex as if the electronic parameters are the numerical average of those found in the complexes CoX_4 and CoY_4. Data in Table 2 compare this approximation.

Table 2.

	Obsd. Dq.	Calcd. Dq.
$[Co(C_6H_5)_3PO)_2Cl_2]$	3270 $cm.^{-1}$	3405 cm^{-1}
$[Co(C_6H_5)_3PO)_2Br_2]$	3180	3265
$[Co(C_6H_5)_3PO)_2(NCS)_2]$	4030	4115
$[Co\{SC(NHCH_2)_2\}_2Cl_2]$ (Ref. *26*)	3390	3390–3530

Lastly, these spectra have yielded the order of these ligands in the nephelauxetic series. This series is based on the order of values of $\beta = B'/B$, where B' is the value of Racah's parameter in the complex and B is the free ion value. Since this parameter measures electron-electron repulsion, it has been argued that the decrease in B on forming a complex is a measure of covalency. Jørgensen introduced the idea that β would be a quantitative measure of this effect. The order of the β values (increasing ionicity) for the complexes of the several ligands studied (*24*, *26*) is



$$\sim -NCO^- < OH^- (C_6H_5)_3PO.$$

It will be noticed that this order roughly parallels the polarizability of the donor atom. It has also been suggested (*27*) that there is a correlation between absorption band intensities and the amount of lowering, ΔB, of the B value from the free cobalt(II) ion value.

The spectra of tetrahedral cobalt(II) complexes are interesting because bands are observed in two widely separated regions, and the spectra are markedly different from those of octahedral cobalt(II). Furthermore, these bands are not usually as simple in shape as those which have been discussed earlier. The simplified energy level diagram for this ion is illustrated in Figure 9. The Tanabe-Sugano matrices for tetrahedral Co(II) are

$$^4A_2(F): \quad -12\,Dq - 15B$$
$$^4T_2(F): \quad -2\,Dq - 15B$$

$$^4T_1(F),\ ^4T_1(P): \quad \begin{vmatrix} -2Dq - 3B & 6B \\ 6B & 8Dq - 12B \end{vmatrix}$$

The lowest energy transition, labeled ν_1, is simply found as $\nu_1 = E(^4T_2) - E(^4A_2) = 10Dq$ and should give Dq directly. However, this band is predicted to be in the vicinity of 3000 cm^{-1} for most complexes and has never been unambiguously observed.

The separation between $^4A_2$ and the $^4T_1$ states is found by evaluation of the above matrix. One finds easily that ν_2 is at $15\,Dq + 7.5\,B - Q$ and ν_3 is at $15\,Dq + 7.5\,B + Q$, where Q is $^1/_2\,[(-6Dq + 15\,B)^2 + 64\,(Dq)^2]^{1/2}$. Observation of the two bands allows the simultaneous solution of these equations and evaluation of both Dq and B.

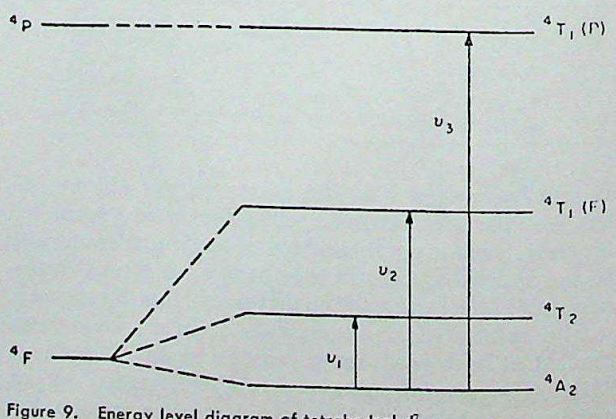


Figure 9. Energy level diagram of tetrahedral d^7.

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The observed spectral bands are usually broad, intense, and show a great deal of structure; this usually requires a choice of an arbitrary band maximum. Spin-orbit coupling is large for Co(II) and this causes part of the splitting, and fields of lower symmetry also contribute to the complexity of the situation. These effects tend to resolve some of the degeneracies indicated in the energy level scheme of Figure 9. No complete calculation of the position of the energy levels in the presence of spin-orbit coupling has been carried out for d^7, although such a calculation for d^8 was most successful (*28*).

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Intrinsic Bond Energies

Bond energy terms are often abused by a confusing and ambiguous terminology (*1*) as well as uncertainty with regard to the zero reference point (*2*, *3*). The most common definition of the bond energy E ((M − X) in a molecule of the type MX_n, is simply the absolute value of the atomic heat of formation of the molecule divided by n. The atomic heat of formation is the binding energy of a molecule and is equivalent to the energy liberated when the atoms in their ground states unite to form the molecule. However the latter definition of bond energy, while widely used, can be misleading in the information it conveys about bond parameters such as bond lengths and force constants. For example, the values for E (C—H) (*2*) in CH_4 and CH_3 are 99.3 and 98.7 kcal/mole respectively, which would lead to the prediction that the C—H bond distances should be longer in the CH_3 molecule than in methane. In point of fact the opposite is true; the C—H distance in CH_4 (*2*) is 1.094Å while that for CH_3 (*4*) is 1.066Å. The reason for this lack of correlation of E with bond length can be attributed to the reference point on which E is based. A reference level for the bond energy based on the ground state atoms clearly does not lead to quantitative correlations with molecular parameters.

It has been pointed out in many places that in accordance with the valence bond treatment of a molecule, the atomic heat of formation of a molecule can be thought of as arising from the sum of two energy terms. The first term is the energy V necessary to place the constituent atoms of a molecule into their appropriate valence states. This can be considered as a promotional energy from the ground state of the atom and thus is endothermic. The valence state of an atom in a molecule can be defined as the hypothetical state in which the free atom would be if the bond involved were broken without any change in the electronic configuration of the atom. The second term contributing to the atomic heat of formation by this formalism is the energy liberated when atoms in their appropriate valence states unite to form a molecule; this is always exothermic for real molecules. Dividing the latter energy term by n for molecules of the type MX_n gives a new bond energy term, which has been called by

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Mulliken the intrinsic bond energy, I. Therefore the atomic heat of formation of a molecule can be written as (3),

$$\Delta H_f = \Sigma V - \Sigma I \qquad (1)$$

where the summation is over all the atoms and bonds of the molecule. This intrinsic bond energy can be regarded as an intrinsic property of the ground state of the molecule, just as bond length and force constant, and thus I can be used for direct correlation with these parameters.

While I is inherently more useful than E, calculation of I requires knowledge of valence state energies of atoms, which are generally not known. Therefore I has not been as widely applied as E. However the intrinsic bond energy concept has pedagogical power in that a greater intuitive grasp of the meaning of bond energy and the range of utility of E can be derived from an understanding of both. Further, as will be discussed in this paper, values for V, and thus I, can be estimated for some simple molecules from thermochemical and spectroscopic data.

Intrinsic Bond Energies From Spectroscopic Data

The valence state energies of the atoms in diatomic molecules can be calculated directly from spectroscopic data by a method first suggested by Pauling (5). In this method the difference between the dissociation energy obtained from a linear Birge-Sponer extrapolation of the vibrational energy levels and from the experimentally determined dissociation energy is attributed to the valence energies of the atoms above their ground states. This procedure is based on the reasonable assumption that diatomic molecules should normally dissociate along a Morse curve and that if the valence state does not change over small vibrations, then a Birge-Sponer extrapolation can be considered to describe the dissociation into valence states. The quantitative relationship needed to calculate the valence energy V is given by equation (2), where $D_0°$ is the experimentally measured dissociation energy from the zero point vibrational level (which for diatomic molecules is simply the atomic heat of formation), and ω_e, $\omega_e X_e$, and $\omega_e Y_e$ are the vibrational frequency and anharmonic contributions, respectively (6).

$$V = \frac{(\omega_e - \omega_e X_e + {}^3/_4\omega_e X_e)^2}{4(\omega_e X_e - {}^3/_2\omega_e Y_e)} - D_0° \qquad (2)$$

The simplest molecules for which intrinsic bond energies can be estimated from valence state energies obtained by the Birge-Sponer extrapolation technique are the diatomic hydrogen compounds. The choice of hydrogen compounds simplifies the calculations since hydrogen can be considered to have essentially a zero valence state energy, and thus only the valence state energy of one atom need be considered for these molecules. Among the diatomic hydrogen compounds of elements atomic number 3–9, the data necessary for application of equation 2 are known for all except BH and NH. The valence state energies calculated by equation 2 are given in Table 1.

The valence state energy calculated by equation 2 for Li in LiH is essentially zero indicating that there is no promotional energy involved in placing the Li atoms into their respective valence states for LiH formation. The next hydrogen molecule is BeH. Since Be in its ground state has the $2s^2$ electronic configuration, an electron must be promoted to a $2p$ orbital before a bond can be formed. However, since a sp hybrid orbital forms a considerably stronger bond than either an s or p orbital alone, the principle of minimizing the energy of a molecule would require that the bond in BeH be essentially 2 $sp\ \sigma - 1s$. The necessity for promotional energy accounts for the appreciable valence state energy of 30 kcal/ mole calculated for Be in BeH. It should be noted that this energy value is less than the 77.5 kcal/mole calculated by Pritchard and Skinner (7), using Moffitt's method (8), for the promotion of the s^2 configuration of Be to the sx pure unhybridized valence state; the latter is different from the hybridized sp valence state. For CH and OH, the valence state energies given in Table 1 are essentially the energies necessary to overcome the electrostatic interaction of the unpaired parallel electrons in the ground state (8) of the C and O atoms.[1] Thus the CH and OH molecules are essentially unhybridized.[2] The zero valence state energy obtained for HF indicates that the fluorine atom in HF is essentially unhybridized.

Although the vibrational constants for BH and NH are unknown so that equation 2 cannot be applied, it is possible to assume reasonably good values for the valence state energies for B and N in these molecules. Since there is only a single p electron in the ground state of the boron atom and therefore no uncoupling energy is necessary and since there appears to be essentially no hybridization in other diatomic hydrides for it is not required, an assumption of zero for V is probably justified. For NH, one must take into account the electrostatic uncoupling energy discussed above for CH and OH. Moffitt obtained a value of 18.2 kcal/mole for this energy (8), and it can be reasonably assumed on the basis of the above discussion that this value is a good approximation for the valence state energy of N in NH.

From the valence state energies the intrinsic bond energies were calculated by equation 1, and are also given in Table 1. As discussed in the introduction, these I values should be related directly to the respective bond lengths. That this is true can be seen from the relationship given in Figure 1, where I is shown to vary linearly with $1/r_0^2$ for the five diatomic hydrides,

[1] Pritchard and Skinner have calculated energies of 7.4 and 11.5 kcal/mole respectively, for the valence energies in CH and OH from spectral data, using the general equations given by Moffitt.

[2] There is a small amount of second-order hybridization in these molecules that contributes some s character to the bonds, but the bonding is predominantly $2p - 1s$.

Table 1. Valence State Energies and Intrinsic Bond Energies for Diatomic Molecules

Hydride	LiH	BeH	BH	CH	NH	OH	FH
$D_0°$ (kcal/mole)	58[a]	51[a]	70[a]	80	85[a]	101.5	134
V (kcal/mole)	0	30	0[b]	7.2	18.2[c]	14.5	0
I (kcal/mole)	58[a]	81[a]	70[a]	87.2	103[a]	116	134

[a] Uncertainty in these values is of the order of 5 kcal/mole.
[b] Assumed to be zero.
[c] Value calculated by Moffitt.

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in which the bonding is $2p - 1s$, while the $2p$ values do not. The intrinsic bond energies for LiH and BeH do not fall on this line but these molecules differ from the others in that the bonding is not $2p - 1s$. While the intrinsic bond energy is always numerically greater than E for molecules in which the isolated atoms require promotional energies, for cases in which there is no promotional energy (LiH, BH and HF) the ordinary bond energy term E is identical to the intrinsic bond energy.

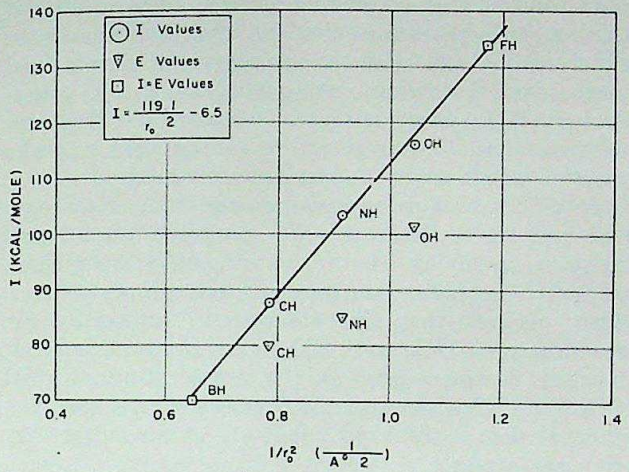


Figure 1. Plot of I versus $1/r^2_0$ for five diatomic hydrides.

Beryllium Hydride Examples

It was shown in the previous section that for diatomic hydrogen compounds containing similar bonding, I can be correlated more satisfactorily with bond properties than can E. The beryllium hydrides provide a further example of the intuitive grasp into the meaning of bond energies that is offered by the intrinsic bond energy concept. Since bond formation in $BeH_2(g)$ must also involve sp orbitals of Be, for identical reasons already discussed for BeH, it can be reasonably concluded that the valence state energies for Be in BeH and BeH_2 are identical, remembering that V is for the isolated Be atom. It also follows that the intrinsic bond energies in these hydrides would be essentially identical since exactly the same type of $2sp\ \sigma - 1s$ bonding is probably present in both. However, the bond energies E are quite different for BeH_2 and BeH; these values are ~76 kcal./mole[3] and ~53 kcal/mole (*2*). From the E values it would appear that the bonds in BeH_2 are considerably stronger than the bond in BeH. This is quite misleading, as is seen by the necessity for essentially equivalent intrinsic bonds in these molecules. On the basis of the predicted identical intrinsic bond strengths one would predict that the bond lengths and force constants in BeH_2 and BeH are identical, while on the basis of the E values one might infer that the BeH bond is longer than the bonds in BeH_2. Although the bond distances in BeH_2 are not known the veracity of the prediction based on I is indicated by the known bond distances for BeF and BeF_2, and also MgF and MgF_2. Whereas the E values for the BeF and MgF bonds in these triatomic fluorides are considerably greater than the E values for these bonds in the diatomic fluorides,[4] the bond distances in these triatomic fluorides (*9*) are identical within experimental error to those of the corresponding diatomic fluorides (*2*).

The discrepancy between models based on E and I stems from the fact that the E values are based on the sum of the internal energies of the isolated atoms and energy terms characteristic of the bond itself. It is the latter energy terms which determine the ground state bond properties of the molecule and not the contribution to the atomic heat of formation by the internal valence energies of the isolated atoms. The experimental dissociation energy of the BeH molecule, and thus the thermodynamic atomic heat of formation is thus lowered by the exothermic release of energy when the dissociated Be atom in its valence state falls to the ground state, an energy step which is independent of intrinsic bond properties. The apparent difference in bond strengths between BeH_2 and BeH based on the E values stems from the fact that there is an identical valence energy term for both molecules but $2I$ in one case and only I in the other; in effect, for the calculation of E values from atomic heats of formation each molecule has a different stake in V.

[3] The standard heat of formation of $BeH_2(g)$ has not been experimentally determined but has been obtained to within an accuracy of about 5 kcal/mole by an empirical method based on the known values for other hydrogen compounds: C. J. Obrien, et al, in "Kinetics, Equilibria, and Performance of High Temperature Systems," G. S. Bahn and E. Zuckowsky, edits., Butterworths Scientific Publications, London, 1960, pp. 5–17.

[4] Cottrell gives a tentative value of 92 kcal/mole for the dissociation energy of BeF; this is based on a value recommended by A. G. Gaydon, "Dissociation of Energies and Spectra of Diatomic Molecules," 2nd ed., London, 1953. Cottrell also gives a tentative value of 74 kcal/mole for the dissociation energy of MgF. The bond energies E for $BeF_2(g)$ and $MgF_2(g)$ are 150 ± 2.5 and 125 ± 2 kcal/mole, respectively, taken from thermochemical data in the "JANAF Interim Thermochemical Tables," Dow Chemical Co., Midland, Mich., Dec. 1961.

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The Inorganic Superoxides

In 1810 Gay Lussac and Thenard (*1*) observed that "potassium combines with twice or even three times as much oxygen as it requires to pass into the state of potash." This was the first recorded evidence of the fact that oxygen can enter into chemical combination in a form other than $O^{=}$. It was not, however, until 1861 that the first really careful quantitative study of these apparently "abnormal oxides" was undertaken. In that year A. V. Harcourt (*2*) obtained, by the combustion of pure potassium metal in air, a yellow compound for which he was able to assign the formula K_2O_4. Harcourt's observations were verified in 1894 by Holt and Sims (*3*). Between the years 1905 and 1907 E. Rengade (*4–6*), using essentially the same method of preparation employed by Harcourt, reported the preparation of Rb_2O_2, Rb_2O_3, and Rb_2O_4, and the corresponding cesium compounds. De Forcand (*7*, *8*), in 1910 and 1914, repeated Rengade's preparative work and also determined the heats of formation and the melting points of the various higher oxides of potassium, rubidium, and cesium. His values for these quantities are listed in Table 1. De Forcand's values for the heats of formation were obtained from experiments performed on the heat of dissociation of the oxide in concentrated sulfuric acid, and are still regarded as the most reliable. Bichowsky and Rossini (*9*) have accepted de Forcand's data in their compilation of the heats of formation of chemical substances. In addition to the preparation of the higher oxides of the alkali metals by combustion of the pure metals in air or oxygen, another method, involving the rapid oxidation of the metals in liquid ammonia, was introduced in 1893 by Joannis (*10*). In 1926 Kraus and Whyte (*11*) perfected the method and prepared K_2O_2 and K_2O_4.

The reaction of hydrogen peroxide with the alkali and alkaline earth metal hydroxides has also been studied as a possible synthetic route to superoxides. The question of whether a reaction occurs between H_2O_2 and HO_2 or the ion of its acid dissociation, O_2^- (the superoxide ion) is in debate. George (*12*) concludes on the basis of experiments of KO_2 dispersed in H_2O_2 solution that no reaction occurs. The validity of this conclusion has been called into question because the experiment dealt with a heterogenous system and mechanisms involving reactions of H_2O_2 and perhydroxyl (HO_2) continue to be suggested. The supposition that HO_2 is a rather strong acid and the reaction is in fact with O_2^- ion is widely held.

Table 1. Heats of Formation and Melting Points of the Higher Oxides of Potassium, Rubidium, and Cesium

Oxide	$-\Delta H_f$ kcal/mole	Mp, °C.
K_2O_2	117	490
K_2O_3	126	430
K_2O_4	135	380
Rb_2O_2	107	570
Rb_2O_3	126	489
Rb_2O_4	137	412
Cs_2O_3	120	502
Cs_2O_4	163	432

In 1952, two Russian investigators, I. A. Kazarnovskii and A. B. Neiding (*13*), proposed an unusual reaction involving the formation of a compound, $K_2O_2 \cdot 2H_2O_2$ (potassium peroxide dihydroperoxidate). They claimed that this compound, formed by the reaction of KOH and H_2O_2, can be kept without marked decomposition at the temperature of solid CO_2 (−78°C). However, at higher temperatures they claimed that it disproportionates into the superoxide, KO_2, and water.

Kazarnovskii and Neiding proposed the following as the main reaction for the disproportionation:

$$3K_2O_2 \cdot 2H_2O_2 \rightarrow 2KO_2 + 4\,(KOH \cdot H_2O) + 3O_2 \qquad (1)$$

They proposed that the main reaction (1), consists of an oxidation of the K_2O_2 by H_2O_2 according to:

$$K_2O_2 \cdot 2H_2O \rightarrow 2KO_2 + 2H_2O \qquad (2)$$

followed by the reaction:

$$2KO_2 + 3H_2O \rightarrow 2(KOH \cdot H_2O) + 1^1/_2O_2 \qquad (3)$$

As a mechanism of the main reaction they write,

$$K_2^{++}O_2^{=}\,(H_2O_2)_2 \rightarrow K^+O_2^- + K^+OH^- + H_2O_2 + OH \qquad (4)$$

wherein the colorless diamagnetic ion $O_2^{=}$ gives up an electron and forms the yellow paramagnetic species O_2^-.

The OH radical then reacts with H_2O_2 to give HO_2, thus

$$H_2O_2 + OH \rightarrow HO_2 + H_2O \qquad (5)$$

and:

$$KOH + HO_2 \rightarrow KO_2 + H_2O \qquad (6)$$

The Russians arrived at most of the above conclusions on the basis of magnetic measurements. They followed the build up of paramagnetism in the reaction mixture as a result of the formation of the paramagnetic KO_2 and subsequent decrease in paramagnetism resulting from the reaction of the KO_2 with H_2O to form the hydroxide and oxygen. Recent work on this reaction at General Dynamics/Electric Boat by Petrocelli has resulted in the isolation of the KO_2 in very high yields and purity (*14*).

Work by Symons (*15*), Wilmarth (*16*), and Forscheimer and Taube (*17*) indicates that in reactions between peroxides and hydroxides, the ozonide species (O_3^-) is important. The Russian mechanism, however, fails to recognize this role of O_3^- in the formation of KO_2 and this impasse needs to be resolved.

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It is to be noted that up to this point no mention of the superoxides of lithium, sodium, or hydrogen has been made. Lithium superoxide (LiO_2) has not as yet been isolated. Claims have been made in the Russian literature for the isolation of LiO_2 but they have not as yet been substantiated (*18*). Thompson and Kleinberg (*19*) have offered convincing evidence that LiO_2 does form when lithium is rapidly oxidized in liquid ammonia at −78°C. A bright lemon-yellow solution is formed, which is characteristic of superoxide formation. In addition they found that the absorption spectra of oxidized liquid ammonia solutions of lithium, sodium, and potassium show all three solutions to have absorption bands close to the same wavelength, 350 mμ. The similarity of the absorption spectra of the lithium solution to that of the sodium and potassium solutions, which are known to contain the respective superoxides, supports the claim that lithium forms a stable superoxide in liquid ammonia solution. However, evaporation of the ammonia did not result in the successful isolation of solid LiO_2.

Sodium superoxide (NaO_2) was prepared for the first time in 1949 by Kleinberg, *et al.* (*20*). They obtained maximum yield of sodium superoxide by subjecting the peroxide to a temperature of 490°C at an oxygen pressure of 298 atmospheres for a period of 100 hr. In 1955, George (*21*, *22*) demonstrated, by means of paramagnetic resonance techniques, that pale yellow samples of commercial sodium peroxide contained approximately 10% sodium superoxide.

Margrave (*23*) has reported some thermodynamic data on NaO_2 which are quite interesting and cast some light on the reasons for the difficulty of obtaining NaO_2 by a direct oxidization process. Margrave considered, thermodynamically, the decomposition of NaO_2 (*s*), i.e.,

$$2NaO_2(s) = Na_2O_2(s) + O_2(g) \qquad (7)$$

Using the low-temperature heat capacity data of Todd (*24*) on NaO_2 and Na_2O_2 he established the free energy functions for the two solids. The thermodynamic data for O_2 (*g*) are well known. The results of his theoretical calculations predict that the equilibrium oxygen pressure is 4 atm at 298°K and 40 ± 20 atm at 600°K. Some actual experimental work carried out by Friedman and Margrave (*25*) indicates that the equilibrium oxygen pressure is actually around 30 atm at 600°K.

The case of the higher oxides of hydrogen is even more interesting and will be briefly considered here. The importance of obtaining hydrogen superoxide (HO_2) as a stable compound is obvious. Not only would it provide a nearly ideal condensed state storage medium for breathing-oxygen, but it also would probably be a very effective high-energy oxidizer in the rocket propellant field. Most claims for the isolation of hydrogen superoxide, which will be written as H_2O_4 in order to avoid confusion with the perhydroxyl radical HO_2, have come from Russian investigators (*26–28*). All such claims appear to have been effectively refuted by recent work (*29–31*). Benson (*29*) has proposed, on the basis of thermodynamic and kinetic evidence, that H_2O_4 can not exist. This question is of such importance in the realm of theoretical and practical chemistry that it is still being actively studied by a small number of investigators.

The tendency of the alkali metals to form higher oxides upon direct combustion with oxygen increases with the ionic radius of the alkali metal ion. In Table 2 are listed the ionic radii of the metal ions and the oxides formed by combustion in an excess of oxygen. The size of the anions increases in the order $O^=$, O_2^-, and $O_2^=$. These facts clearly suggest that increasing cation size is essential to promote crystal stability by permitting inclusion of the larger $O_2^=$ and O_2^- ions (*32*).

Table 2. Stable Forms of the Alkali Metal Oxides Produced by Direct Combustion of the Metals in an Excess of Oxygen

Metal	Oxide formed	Ionic radius Å (*26*)
Li	Li_2O	0.60
Na	Na_2O_2	0.95
K	KO_2	1.33
Rb	RbO_2	1.48
Cs	CsO_2	1.69

The structure of the superoxide ion is of interest and should be considered. For many years following their discovery the superoxides were considered to be tetroxides having a formula as written in Table 1, i.e., M_2O_4. Since sulfur forms tetrasulfide compounds the above formulation for the superoxides appeared quite reasonable. The electronic structure of the "tetroxide ion" was pictured as shown in Figure 1*a* (*33*).

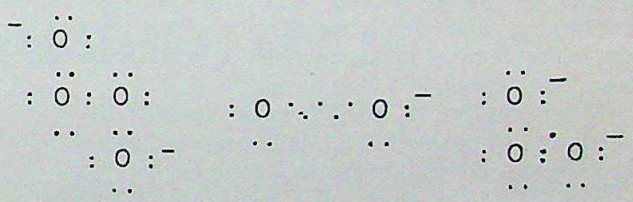


Figure 1. Electronic structure of O_4^- (tetroxide ion), O_2^- (superoxide ion), and $O_3^=$ (sesquioxide ion), reading from left to right.

In 1931 Pauling (*34*) introduced the concept of the three-electron bond and suggested the possibility that the superoxide ion might indeed be an O_2^- species species containing a three-electron bond. The structure of this ion is shown in Figure 1*b*. Pauling reasoned that if the formulation of the superoxide ion is actually as shown in Figure 1*b* then the compounds containing this ion should display paramagnetism by virtue of the fact that the three-electron bond contains one unpaired electron. On the other hand one should expect no paramagnetism if the oxygen is in the form of a tetroxide ion. Following a suggestion by Pauling, Neuman (*35*), in 1934, made a study of the magnetic properties of potassium superoxide and found that it is indeed paramagnetic.

Final confirmation of the existence of the O_2^- ion resulted from the X-ray studies of Kossatochkin and Kotov (*36*), in 1936 and Helms and Klemm (*37*, *38*) in 1939. Their X-ray data demonstrated that at room temperature superoxides possess a tetragonal face-centered lattice of the calcium carbide type. Carter, Margrave and Templeton (*39*) later showed that KO_2 undergoes a transition in the region 60 to 100°C, to a cubic form. The elementary cell contains four alkali metal atoms and eight oxygen atoms. The distance

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Table 3. Summary of Important Properties of Inorganic Air Revitalization Materials

Compound	Formula	Lb O_2/lb compound	Lb generated base/lb compound	Use as air revitalization system: O_2 source	Use as air revitalization system: CO_2 pick up	Remarks
Lithium ozonide	LiO_3	0.73	0.44	Yes	Yes	1
Sodium ozonide	NaO_3	0.56	0.56	Yes	Yes	2
Potassium ozonide	KO_3	0.46	0.65	Yes	Yes	3
Lithium superoxide	LiO_2	0.61	0.62	Yes	Yes	4
Sodium superoxide	NaO_2	0.43	0.73	Yes	Yes	5
Potassium superoxide	KO_2	0.34	0.79	Yes	Yes	6
Calcium superoxide	$Ca(O_2)_2$	0.46	0.71	Yes	Yes	7
Sodium chlorate (candles)	$NaClO_3$	0.40	None	Yes	No	8
Hydrogen peroxide	H_2O_2	0.47	None	Yes	No	9
Hydrogen superoxide	H_2O_4	0.73	None	Yes	No	10

Remarks

1. As yet unprepared, evidence is far from conclusive that it cannot be prepared. Outstanding O_2 source.
2. Prepared. Conflicting reports concerning its stability.
3. Prepared. Conflicting reports concerning its stability.
4. Unsubstantiated Russian claims for its preparation and stabilization at room temperature.
5. Commercial route for its preparation available. Expensive.
6. Commercial route for its preparation available. Widely used.
7. Produced in low yield. Highly desirable due to high melting point of $Ca(OH)_2$.
8. Widely used as emergency O_2 source.
9. Liquid solutions. Requires auxiliary chemical for CO_2 removal.
10. Essentially unsubstantiated Russian claims. Highly attractive as high energy oxidizer.

between adjacent oxygen nuclei in the superoxide ion is 1.28 ± 0.07 Å. This inter-atomic distance is in good agreement with the calculated value of 1.24 Å (*33*), expected for the single bond plus the three-electron bond. At the present time, therefore, there is little doubt that the electronic structure of the superoxide ion is as illustrated in Figure 1*b*.

One of the interesting and important questions concerning superoxide chemistry has been whether or not in the course of the decomposition of the superoxides a stable compound M_2O_3 is formed.

Many workers (*7*, *40*, *41*) have reported the preparation of the oxide M_2O_3. The proposed structure of the sesquioxide ion is shown in Figure 1*c*.

In 1933 Centerszwer and Blumenthal (*41*) reported results of a thermal decomposition study of the MO_2, M_2O_3, and M_2O_2 compounds of potassium, rubidium, and cesium. They measured equilibrium pressures at various temperatures in the range 198 to 580°C. They did not, however, report equilibrium pressure data as a function of sample composition at a given temperature. Thus, pressure-composition isotherms cannot be constructed from their data and a definite conclusion as to which oxides form in the course of the thermal decomposition of the superoxide cannot be reached. In addition the dissociation pressures which they report are extremely high as compared to the values obtained in a subsequent similar study made by Kazarnovskii and Raikhshtein (*42*). Possible reasons for the apparent abnormality of Centerszwer's results have been advanced by Petrocelli (*43*).

Helms and Klemm (*37*, *38*) carried out X-ray studies of samples which were analyzed as K_2O_3. They found that this material does not contain any $O_3^=$ ion, and is actually a mixture of superoxide and peroxide, $KO_2 + K_2O_2$. Further, in 1947, it was quite definitely established by Kazarnovskii and Raikhshtein (*42*) that in the thermal decomposition of potassium superoxide below its melting point, K_2O_3 is not formed as an intermediate oxide. Their results, which disagree with those of Centerszwer, showed that on the removal of oxygen from the superoxide at a constant temperature, the pressure remains constant until the composition of the peroxide, K_2O_2, is reached, where a sudden drop in pressure occurs. On the basis of this evidence it seems quite conclusive that K_2O_3 does not form. This study was repeated in part by Petrocelli (*43*) and the results were found to be in good agreement with those of Kazarnovskii and Raikhshtein. Present-day interest in alkali and alkaline earth superoxides is quite high, due primarily to the potential which these compounds possess as inorganic air revitalization materials.

Table 3 summarizes some of the important properties of compounds useful for air revitalization purposes. A review of the chemistry of the inorganic ozonides has been recently published (*44*).

Acknowledgment

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Textbook Errors, 42

The Thermal Stability of H_2Se

In the past ten years several textbooks[1] have stated that hydrogen selenide may be readily broken down thermally to the constituent elements, and 160°C was even quoted as the temperature at which decomposition is measurable. This result, which does not appear to be documented in any of the texts, is at variance with the larger, older compilations usually described as authoritative.[2-3]

Recently we had occasion to establish experimentally that, in contrast with the textbook statements, hydrogen selenide is in fact quite stable thermally. No decomposition was observed at 280°C when we attempted to prepare a selenium film for another investigation by taking advantage of the alleged instability of the hydrogen selenide.

A conventional high vacuum apparatus was used for an experimental test. Hydrogen selenide was prepared by the action of 10% sulfuric acid on iron selenide, the gas was roughly dried by passage through a trap filled with anhydrous magnesium perchlorate and collected in a trap at liquid nitrogen temperature. It was then purified by repeated distillation-sublimation in the conventional manner and sent to storage.

The reactor was essentially a large Pyrex U-tube, to which was attached an all glass circulating pump, a thermocouple well and a manometer sensitive to 0.2 mm. The reactor was surrounded by an oil thermostat which permitted temperature control within the reactor to ±0.5 °C. The reactor was held at 280°C ±0.5° during all experiments.

In a typical experiment, hydrogen selenide was introduced into the hot reactor up to a predetermined pressure, and its behavior observed over a period of time. The initial H_2Se pressure was varied between approximately 5 and 120 mm of Hg. *In no instance* was there any evidence of decomposition over a three hour period.

On the other hand, the introduction of approximately equal quantities of air dried over magnesium perchlorate into the reactor containing the hydrogen selenide caused rapid deposition of grey selenium on the cooler parts of the reactor. This occurred at all pressures, but faster at the higher ones.

Thus it may be concluded that contrary to the texts, pure hydrogen selenide is stable at least to 280°C and that the low temperature reaction, described by them, is probably due to the presence of impurities such as oxygen.

Suggestion of material suitable for this column and guest columns suitable for publications directly are eagerly solicited. They should be sent with as many details as possible, and particularly with references to modern textbooks to Karol J. Mysels, Department of Chemistry, University of Southern California, Los Angeles 7, California.

[1] Since the purpose of this column is to prevent the spread and continuation of errors and not the evaluation of individual texts, the source of errors discussed will not be cited. The error must occur in at least two independent standard books to be presented.

[2] Mellor, J. W., "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Longmans Green and Co., New York, 1930, Vol. X, p. 759.

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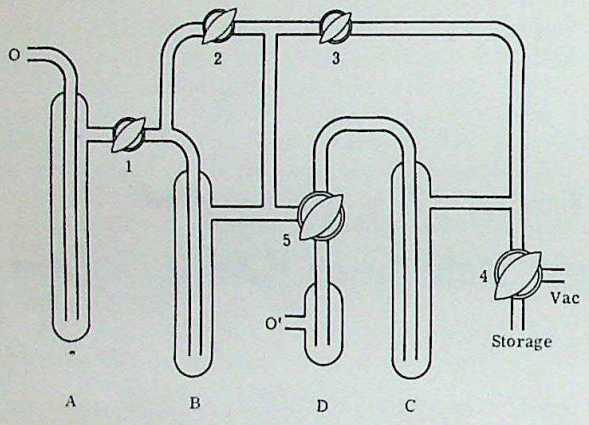
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Praseodymium Oxide-Oxygen Generator

During the course of an investigation of the phase diagram of the Pr-O system,[2-4] the relative ease with which oxygen could be removed from and combined with the oxides of praseodymium became apparent. The possibility of using this system as a source of research quantities of oxygen naturally occurred. In addition, the possibility of the regeneration of the oxide reactant *in situ* was appealing. The simple apparatus shown in the figure was constructed to test the idea.



Trap *A* in the figure contained glass helixes and was used to prevent water vapor from entering the system. Trap *B* was constructed from fused silica (Vycor may be used) and contained approximately 20 grams of Pr_6O_{11}. Trap *C* contained activated charcoal and was used to adsorb the generated oxygen. Trap *D* was a small Pyrex bubbler filled with a few ml of dibutyl phthalate; the bubbler was used to monitor the flow of air through trap *B* during the regeneration process. All stopcocks were of a high vacuum type.

The oxide was conditioned initially by removing all impurity gases which were sorbed chemically or physically.[5] A mercury diffusion pump provided the necessary vacuum, and vertical tube furnaces were used as the heating elements. Trap *C* was heated at 200°C for several hours to aid in the removal of sorbed gases. Trap *B* containing the oxide *in vacuo* was heated to 900°C and the Pr_6O_{11} was regenerated as mentioned below.

At the beginning of the generation all stopcocks were open except no. 1, and the system was evacuated. To generate oxygen, stopcock no. 4 was opened to the previously evacuated storage flask; stopcock no. 3 was closed and the temperature of the tube furnace around trap *B* was raised to between 700–900°C. Oxygen evolved slowly under these conditions and reached an equilibrium pressure of about 150–160 mm. after a few minutes. The composition at this point is $\sim PrO_{1.71}$. To reduce the oxide further to a composition nearer $PrO_{1.5}$, a Toepler pump may be conveniently used to pump the oxygen from the generator into the storage vessel. More simply trap *C* may be cooled with liquid air to cause the oxygen to adsorb on the charcoal, after which the oxygen can be distilled into the storage flask at a pressure greater than 150 mm. In this case stopcocks nos. 3 and 5 are closed and no. 4 is open to the storage vessel.

To regenerate the oxide (Pr_6O_{11}), the temperature (900°C) was maintained and stopcocks nos. 4 and 5 were closed; air was carefully introduced through no. 1 (no. 2 open) until atmospheric pressure was attained inside the system. Stopcocks nos. 2 and 3 were then closed and no. 5 was opened to the atmosphere through O′. Compressed air from a service line was blown slowly through the system via the path O-A-1-B-5-O′. The flow of air was monitored with bubbler *D*. The temperature of the furnace around trap *B* was then reduced to 450°C at the rate of about 5°C/min. At 450°C the system was allowed to equilibrate for 15 minutes after which time the temperature was reduced to 200°C and the system subsequently evacuated. The generator was then ready to produce more pure oxygen and the cycle was repeated.

The purity of the generated oxygen was checked by analyzing samples of the gas with a Bendix Time-of-Flight mass spectrometer. Mass numbers through 50 were scanned, and there was no indication that any other gaseous components were present except oxygen.

The generation of oxygen using praseodymium oxide has several advantages: (1) The starting material may be regenerated *in situ* by simple and economical means. (2) The initial investment of Pr_6O_{11} is never lost as it is in the case of $KMnO_4$, for example. (3) The actual time spent by the operator to perform the generation is small; the generation needs only a minimum of supervision since the evolution of gas is not necessarily rapid and is easily controlled. (4) The generation is relatively safe although caution should be exercised. The gas pressure never exceeds 150–160 mm. at temperatures below $\backsim$ 900°C. When using the liquid

This research was supported by the United States Air Force through the Air Force Office of Scientific Research of the Air Force Research and Development Command, under contract no. AF 18(603)-45. Reproduction in whole or in part is permitted for any purpose of the United States government.

[1] Present address: Lewis Research Center, 21000 Brookpark Road, Cleveland 35, Ohio.

[2] Ferguson, R. E., Guth, E. D., and Eyring, L., *J. Am. Chem. Soc.*, 76, 3890 (1954).

[3] Honig, J. M., Clifford, A. F., and Faeth, P. A., *J. Inorg. Chem.*, in press.

[4] Faeth, P. A., PhD thesis, Purdue University, 1961.

[5] Faeth, P. A., "Adsorption and Vacuum Technique," University of Michigan Press, Ann Arbor, Mich., in press.

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nitrogen trap method, should the liquid nitrogen become depleted by an oversight, the oxygen adsorbed on the charcoal would desorb and recombine with the oxide and not build up an excessive pressure. To guard against a power failure (which would lower the oxide temperature rapidly) and subsequent liquid nitrogen depletion (which would raise the gas pressure), a safety device such as a mercury bubbler could be installed in the system. (5) The equipment needed for the generation is conveniently found in most laboratories with the possible exceptions of the silica tube and the Toepler pump.

The possibility of using the reduced oxide (Pr_2O_3) as a "getter" for oxygen has not been extensively studied in this laboratory but this application seems promising. A sample of the reduced oxide, maintained at 400–450°C in the above system, removed completely a sample of oxygen which had been generated at higher temperatures. The oxide might conveniently be used to remove oxygen from gas samples during certain gas analyses. A suggested additional use of the oxide is as a source of oxygen at relatively constant pressure to be used in conjunction with the constant oxygen pressure studies of other systems.

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Inorganic Reaction Mechanisms by Volumetric Analysis

Oxidation of iodide ion

Conventional volumetric exercises are too commonly related to such determinations as solute concentration in aqueous solution, equivalent weights, or empirical formulas. Yet with little effort or the need for elaborate equipment, these same experiments can often be usefully employed to illustrate more fundamental chemical principles. This is well illustrated in the case of the Andrews' titration[1, 2] which students normally use directly in the estimation of iodide, or indirectly in the estimation of such materials as the salts of tin, copper, and mercury, and certain higher oxides, e.g., the dioxides of barium, lead, and manganese.

Many chemical reactions proceed in a number of intermediate steps, the sum of which can be represented by an over-all chemical equation. Facile demonstration of this important concept of stepwise reactions is not always possible. Recently,[3] it has been shown that the Andrews' method provides a relatively simple means of exposing the two-step oxidation of the iodide ion (I^-) to iodine (I^+) in concentrated hydrochloric acid solution with a variety of oxidizing agents. The two steps are:

$$I^- \rightarrow {}^1/_2I_2 + e^- \qquad (1)$$

and

$${}^1/_2I_2 + 2Cl^- \rightarrow ICl_2^- + e^- \qquad (2)$$

The over-all reaction is represented by

$$I^- + 2Cl^- \rightarrow ICl_2^- + 2e^- \qquad (3)$$

Volumetric Studies

In a typical group experiment, varied weights of reagent grade chromium(VI) oxide were treated with a known excess (25 ml) of potassium iodide (0.0996 *M*) in concentrated hydrochloric acid. After complete reaction, extraction with carbon tetrachloride allowed for separate titration of the iodine (I_2) produced (in the carbon tetrachloride layer) and of unreacted iodide (I^-) (in the aqueous layer) with standard (0.025 *M*)

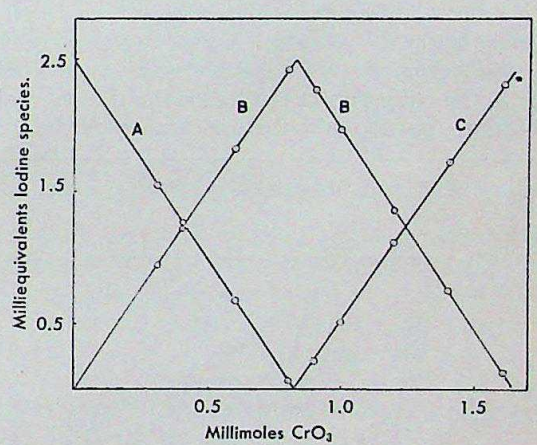


Figure 1. Oxidation of the iodide ion by chromium(VI) oxide. *A*, I^-; *B*, I_2; *C*, ICl_2^-.

Table 1. Oxidation of the Iodide ion by Chromium(VI) Oxide. (Showing Iodide (I^-) and Iodine (I_2) Present in Terms of ml Potassium Iodate (0.025 *M*))

Weight CrO_3 g	Titer KIO_3 (without CCl_4 partition) ($I^- + I_2$) ml	Titer KIO_3 (CCl_4 layer) (I_2) ml	Titer KIO_3 (aqueous layer) (I^-) ml
0.03	40.4	9.38	30.9
0.04	37.6	12.3	25.25
0.06	31.8	18.3	13.55
0.08	25.6	24.4	1.25
0.09	22.72	22.83	0.05
0.10	19.8	19.75	0.1
0.12	13.65	13.7	0.05
0.14	7.75	7.63	0.1
0.16	1.45	1.42	0.05

[1] Andrews, L. W., *Z. anorg. Allge.Chem.*, **36**, 76 (1903).
[2] Andrews, L. W., *J. Am. Chem. Soc.*, **25**, 756 (1903).
[3] Moody, G. J., and Thomas, J. D. R., *J. Inorg. and Nucl. Chem.*, in press.

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potassium iodate. As a check on the total reactive species of iodine, duplicate runs without carbon tetrachloride partition, were carried out.

The group was then instructed to present the results in tabular and graphical form and to interpret and comment thereon.

Table 1 shows that the iodine (I_2) formed increases from zero to a maximum, while the formation of iodine (I^+) is temporarily suppressed. Figure 1 illustrates the relationship between steps (1) and (2) even more dramatically, wherein the iodide (I^-) ion concentration becomes zero and iodine (I_2) production reaches a maximum before step (2) can come into play. Iodine (I^+) finally attains a maximum concentration when the iodine (I_2) concentration has fallen to zero.

It must be emphasized that the above evidence alone does not preclude the premature participation by reaction (2) — the iodine (I^+) being removed by

$$ICl_2^- + I^- \rightarrow I_2 + 2Cl^- \qquad (4)$$

The above has also been shown to occur with potassium dichromate, lead dioxide, manganese dioxide, and potassium iodate.[3]

Spectrophotometric Studies

The practical investigation can be extended by students having access to spectrophotometric equipment since supporting evidence for the presence of the various species of iodine can be obtained. Iodine (I_2), iodide (as I_3^-), and iodine (I^+) (as ICl_2^-) are known to have absorption maxima at 22,800 cm^{-1},[3] 28,400 cm^{-1},[3] and 29,200 cm^{-1},[3,4] respectively, in an aqueous solution of hydrochloric acid. Figure 2 clearly indicates good resolution of these species present at various stages of the oxidation of the iodide ion (I^-) by potassium iodate, particularly the appearance of the ICl_2^- absorption maximum at 29,200 cm^{-1} (curve *C*) and the disappearance of the I_3^- absorption at 28,400 cm^{-1} (curve *B*) and of the I_2 absorption at 22,800 cm^{-1} (curve *D*).

The spectra shown in Figure 2 were recorded on tenfold dilutions in a concentrated hydrochloric acid/deionized water mixture (50:65), of solutions prepared by mixing measured volumes of potassium iodate (0.025 *M*) with 25 ml potassium iodide (0.0996 *M*) and 50 ml concentrated hydrochloric acid. Prior to dilution, the solutions were made up to 115 ml with deionized water except that the undiluted volume of the solution used for curve *D* was 125 ml.

[4] Gillam, A. E., and Morton, R. A., *Proc. Roy. Soc.*, A 132, 152 (1931).

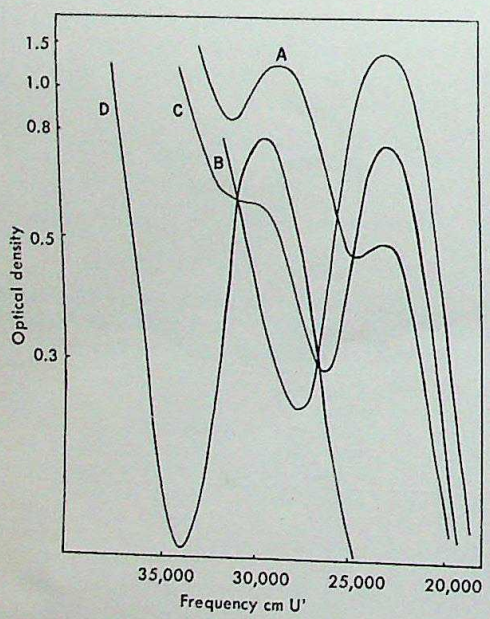


Figure 2. Absorption spectra obtained by adding potassium iodate (0.025 *M*) to 25 ml potassium iodide (0.0996 *M*). *A*, 5 ml KIO_3; *B*, 20 ml KIO_3; *C*, 35 ml KIO_3; *D*, 50 ml KIO_3.

Thermodynamic Considerations

The above practical exercises can very usefully be preceded and augmented by calculations involving oxidation-reduction potentials and free energies, followed by an assessment of the thermodynamic probability of the reactions.

For example, Latimer[5] quotes the following $E°$ values for the two stages corresponding to the iodide oxidation:

$$I^- = {}^1/_2I_2 + e^-; \quad E° = -0.5355 \text{ volt} \qquad (5)$$

$$2Cl^- + {}^1/_2I_2 = ICl_2^- + e^-; \quad E° = -1.06 \text{ volt} \qquad (6)$$

Combination of equation (5) with the data for the chromium (III):chromium (VI) system

$$2Cr^{3+} + 7H_2O = Cr_2O_7^{-2} + 14H^+ + 6e^-; \quad E° = -1.33 \text{ volt} \qquad (7)$$

gives

$$Cr_2O_7^{-2} + 6I^- + 14H^+ = 3I_2 + 2Cr^{+3} + 7H_2O; \quad E° = +0.7945 \text{ volt} \qquad (8)$$

Since $\Delta F° = -n\mathfrak{F}E°$, $\Delta F°$ for reaction (8) is

$$-\frac{6 \times 96{,}500 \times 0.7945}{4.18} = -110{,}100 \text{ cal}$$

The large negative value for $\Delta F°$ indicates that reaction (8) is spontaneous in the direction written.

Similarly, the second step, that is, the oxidation of iodine (I_2) to iodine (I^+) by dichromate ion can be represented by combining equations (6) and (7) to give

$$Cr_2O_7^{-2} + 3I_2 + 14H^+ + 12Cl^- = 6ICl_2^- + 2Cr^{+3} + 7H_2O; \quad E° = +0.27 \text{ volt} \qquad (9)$$

for which $\Delta F°$ is −37,410 cal., a value much less negative than that calculated for reaction (8). Even so, reaction (9) is spontaneous in the direction written.

Similar calculations may be made for lead dioxide, manganese dioxide, and potassium iodate as oxidizing agents from the following $E°$ data:[5]

$$Pb^{+2} + 2H_2O = PbO_2 + 4H^+ + 2e^-; \quad E° = -1.455 \text{ volt} \qquad (10)$$

$$Mn^{+2} + 2H_2O = MnO_2 + 4H^+ + 2e^-; \quad E° = -1.23 \text{ volt} \qquad (11)$$

$${}^1/_2I_2 + 3H_2O = IO_3^- + 6H^+ + 5e^-; \quad E° = -1.195 \text{ volt} \qquad (12)$$

These reveal a similar spontaneous character.

The calculations and experiments outlined can be extended to the oxidation of the iodide ion by a range of other oxidizing agents for which $E°$ values are available.

[5] Latimer, W. M., "Oxidation Potentials," 2nd ed., Prentice-Hall, Inc., New York, 1952, p. 340.

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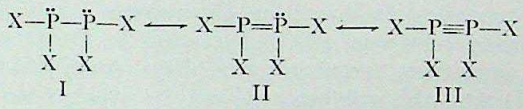
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Chemistry of Diphosphorus Compounds

In a recent review of the chemistry of phosphorus (*1*) less than a dozen pages from more than nine hundred deal with compounds containing phosphorus-phosphorus bonds other than hypophosphoric acid. Although diphosphorus compounds have been known for almost 150 years, it has been only recently that an interest in them has developed. Much of the work reviewed here has been published in the last ten years. It would appear that the chemistry has now progressed to a stage where a certain amount of systemization may be applied to it. The present article is an attempt to provide such a systemization as well as to point out some of the more interesting aspects of diphosphorus chemistry.

Tricovalent Diphosphorus Compounds. The basic structure of this class of compounds is that of two phosphorus atoms joined by a sigma bond, with each in turn surrounded by two substituent groups and an unshared pair of electrons(I). In addition, resonance forms can be written ((II), (III)) in which the 3*p* and 3*d* orbitals of the phosphorus



I II III

atoms form d_π-p_π bonds, giving multiple bond character to the P—P bond. Burg (*2*) has attributed the formation of tetramethyldiphosphine from dimethylaminodimethylphosphine and dimethylphosphine

$$(CH_3)_2PN(CH_3)_2 + (CH_3)_2PH \rightarrow (CH_3)_2PP(CH_3)_2 + (CH_3)_2NH$$

to the fact that two pi bonds can form in the diphosphorus compound, but only one in the aminophosphine. He estimated the other bond energies in the molecules to be comparable and assigned the heat of the reaction ($\Delta H = -1.79$ kcal mole^{-1}) to the formation of the second pi bond. This bond is far weaker than the pi bond in olefins (*ca.* 60 kcal mole^{-1} (*3*)) and should present little barrier to rotation. In hydrazine, in which pi-bonding is impossible, the barrier is 2.80 kcal mole^{-1} (*4*). Other properties of diphosphorus compounds are consistent with a structure in which canonical form I predominates.

Biphosphine is generally formed as a by-product in the preparation of phosphine. Although much less basic than hydrazine, it forms adducts with diborane and with boron trifluoride (*5*). Biphosphine is rather unstable thermally. It decomposes in liquid ammonia (*6*) or simply on warming to room temperature (*7*), producing polymeric hydrides of uncertain structure.

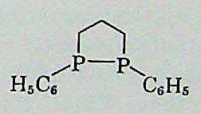
Substituted diphosphines are far more stable than biphosphine itself. As early as 1888, Dörken (*8*) produced tetraphenyldiphosphine by the elimination of hydrogen chloride from diphenylphosphine and diphenylchlorophosphine. In a recent investigation of this reaction, Kuchen and Buchwald (*9*) reported yields of 80%. Maier (*10*) prepared a mixed tetraalkyl derivative, 1,2-dimethyl-1,2-diethyldiphosphine, by reduction of the corresponding disulfide with zinc or tertiary phosphines. Tetramethyl-(2), 1,1-dimethyl-2,2-*bis*(trifluoromethyl)- (*11*), and *tetrakis*(trifluoromethyl)diphosphine (*12*) have also been prepared. The last of these exhibits remarkable stability for a diphosphorus compound.

A rather unusual cyclic diphosphine (IV) has recently been reported (*13*). It is prepared by treatment of 1,2-dibromoethane with the di-lithium derivative of P,P′-diphenyltrimethylenediphosphine:

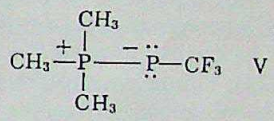
$$H_5C_6—P(Li)—(CH_2)_3—P—LiC_6H_5 + BrCH_2CH_2Br \rightarrow$$

$$H_5C_6—\overline{P(CH_2)_3P}—C_6H_5 + CH_2{=}CH_2 + 2LiBr$$

Another novel diphosphine, 1,1,1,-trimethyl-2-trifluoromethyldiphosphine (V) has been the subject of a recent note (*14*). It forms readily when the cyclopolyphosphines $(PCF_3)_4$ and $(PCF_3)_5$



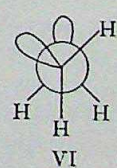
IV



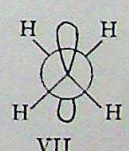
V

are treated with trimethylphosphine. The material dissociates to the original reactants quite readily, indicating the unsymmetrical structure. If this structure is the correct one, it appears unique inasmuch as it is a zwitterion with a phosphonium ion and a phosphide ion in the same molecule. Similar products are formed by the reaction of the cyclophosphines with trimethylamine.

On the basis of the number of Raman-active modes, a *gauche* configuration (VI) has been assigned to diphosphine rather than the expected *trans* configuration (VII) (*15*).



VI



VII

This structure is also indicated by infrared spectroscopy (*16*) and probably should be interpreted as resulting from a low energy barrier to rotation rather than a fixed *gauche* configuration. With essentially free rotation, the molecule would exhibit C_2 symmetry.

The Raman spectrum indicates a force constant of 1.85×10^5 dynes cm.$^{-1}$ and an interatomic distance

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of 2.11 Å for the P—P bond in diphosphine (*15*).

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Two diphosphorus tetrahalides are known. The iodide was probably first prepared as early as 1813 by Gay-Lussac (*17*), who fused the elements to obtain a crude product. Early workers prepared it in a number of ways, among which were the reaction of phosphorus(III) chloride with methylmagnesium iodide (*18*), the reduction of the triiodide with mercury (*19*), the oxidation of phosphine with iodine (*20*), and the reaction of iodine with phosphorus(III) oxide (*21*). The first workers to report preparation of the compound in a good state of purity were Germann and Traxler (*22*), who obtained it from stoichiometric quantities of the elements dissolved in carbon disulfide previously freed from sulfur by shaking with mercury. More recently, an improved synthesis from iodine and red phosphorus has been claimed (*23*).

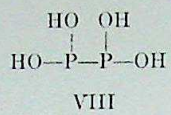
Diphosphorus tetraiodide is one of the few diphosphorus compounds for which the exact structures have been determined. X-ray studies (*24*) have shown that the molecule has the *trans* configuration in the solid state, with the following parameters: ∠PPI = 93°57′, IPI = 102°18′, P—P bond = 2.21 Å, P—I bond = 2.47 Å. The P—P bond length is that expected for a single covalent bond (r_{cov} = 1.10 Å) (*1*).

Little is known about the other diphosphorus tetrahalides. An early attempt to produce diphosphorus tetrachloride by chemical replacement failed. Heating a mixture of diphosphorus tetraiodide with silver chloride produced phosphorus(III) chloride and a phosphorus-containing residue (*25*). Besson and Fournier (*26*) claimed the preparation of the chloride by reduction of phosphorus(III) chloride with hydrogen in an electrodeless discharge, but this report remained unconfirmed for a long period of time. Gutmann (*27*) passed an electrodeless discharge through samples of hydrogen saturated with the vapors of phosphorus(III) chloride, phosphorus(III) bromide, and phosphoryl chloride, respectively. In each case, "red phosphorus" was obtained along with unidentified liquid products. Finch (*28*) produced diphosphorus tetrachloride by reduction of phosphorus(III) chloride with a high-voltage mercury arc. Extensive decomposition occurred with the formation of red and yellow deposits on the walls of the reaction tube and phosphide coatings on the mercury. A small quantity of liquid was obtained, which condensed as crystals at −45°C, and melted sharply at −35° to −34°C. The colorless liquid thus produced decomposed at room temperature, leaving a yellow, non-volatile solid and phosphorus(III) chloride. The liquid fumed in air and reacted vigorously with water. It gave a good analysis for $(PCl_2)_n$, and molecular weight determinations gave values of 191 and 194 (calc. for n = 2, 204).

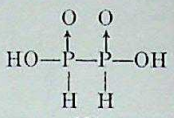
Preliminary attempts to produce the tetrafluoride via reaction of the chloride with Swarts-type reagents have proved unsuccessful (*28*). The tetrabromide is also unknown.

The hydrolysis of diphosphorus tetraiodide has been reported to yield hypophosphorous acid, phosphorous acid, phosphoric acid, phosphine, "$P_{12}H_6$," and hydriodic acid (*29*). Oxidation of the hydrolysate resulted in the transformation of 24% of the phosphorus into hypophosphoric acid. On this basis, a $P_2(OH)_4$ intermediate was postulated.

In a preliminary communication, Baudler (*30*) described the characterization of a new diphosphorus acid in the hydrolysis mixture. Her identification was based on the reducing capacity of the solution in acidic and basic media, the susceptibility to air oxidation, and the fact that paper chromatography indicated that a new acid species was present. Like phosphorous acid, the new acid presumably is capable of existence in two tautomeric forms, dibasic and tetrabasic:



VIII



IX

The preparation of diphosphate(II, II) esters,[1] $(RO)_2PP(OR)_2$, has been claimed in a patent (*32*). It is claimed that treatment of a diarylchlorophosphate(III) with metallic sodium in hot xylene results in the formation of tetraaryldiphosphate(II, II) esters and sodium chloride. The only compound specifically mentioned was tetracresyldiphosphate(II, II), which was described as a straw-yellow, oily liquid at room temperature with certain properties as a film strengthening agent. No methods of characterizing the compounds were given.

Alcoholysis of diphosphorus tetraiodide leads largely to polymeric products, but small amounts of diphosphate(II, II) esters have been tentatively identified on the basis of the ultraviolet absorption spectra (*33*). Similarly, amines cause the formation of insoluble, polymeric products (*33*, *34*), but amidophosphates(II, II) can be prepared by coupling with sodium (*34*).

Tetracovalent Diphosphorus Compounds. In view of the many references in the literature to the preparation, properties, and structure of hypophosphoric acid, a review of this subject need not be attempted here. The interested reader is referred to Van Wazer's monograph (*1*) for a comprehensive survey of the literature prior to 1958.

The preparation of hypophosphate esters is of some interest inasmuch as the earlier syntheses (*35*, *36*) of "hypophosphate esters" have been shown to lead in fact to diphosphate(III, V) esters (isohypophosphates) (*37*):

$$2(RO)_2PO^- + X_2 \rightarrow (RO)_2P(O)OP(OR)_2 + 2\,X^- \quad (X = Br, Cl)$$

Apparently the first preparation of a true hypophosphate ester was that by Baudler (*38*) who prepared tetramethyldiphosphate(IV, IV) by methylation of anhydrous hypophosphoric acid with diazomethane. A more general method involves the coupling of two moles of dialkylchlorophosphate(V) with sodium (*39*). The structures of these esters, as well as those of the free acid and the isohypophosphates of previous workers, have been assigned on the basis of their Raman spectra (*37*, *40*). The formation of the diphosphate (III, V) esters by the oxidation of dialkylphosphates (III) with halogen can be rationalized in terms of the

[1] Nomenclature is based on the oxidation state of the phosphorus (*31*) in the absence of a better method. The naming of polyphosphous compounds is currently being studied by the ACS Inorganic Subcommittee on Phosphorus Nomenclature.

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addition of a mole of halogen to the dialkylphosphate(III) ion followed by nucleophilic attack of another dialkylphosphate(III) ion on the acid halide thus formed:

$$(RO)_2PO^- + Br_2 \rightarrow Br^- + (RO)_2P(O)Br$$

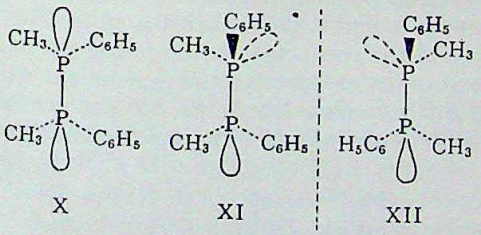
$$(RO)_2P(O)Br + (RO)_2PO^- \rightarrow (RO)_2P(O)OP(OR)_2 + Br^-$$

Esters of thiohypophosphoric acid (dithiodiphosphoric (IV, IV) acid) have been claimed in a patent (*32*), but no properties were given. The dimethylamides of both hypophosphoric and thiohypophosphoric acid have been prepared, but little is known of their chemistry as yet (*34*).

Diphosphine chalcogenides can be prepared by oxidation of the corresponding diphosphine with air to form the dioxides, or sulfur to form the disulfides (*9*). The preparation of tetralkyldiphosphine disulfides can also be accomplished via the Kabachnik-Shepeleva reaction (*quid vide infra*). Treatment with one or two moles of a tertiary phosphine results in the diphosphine monosulfide or the diphosphine, respectively (*41*).

Optical Activity in Diphosphines. Diphosphines of the type RR′PPRR′ and their chalcogenides should exist in the form of a *meso* isomer and a pair of *d*, *l*-isomers. The isomers containing tricovalent phosphorus would be expected to be quite labile because of the facility of inversion about the phosphorus atom. Presumably the addition of a fourth group could hinder such inversion and stabilize the isomers.

In the case of the diphosphine disulfides, Maier (*10*) has succeeded in separating the *meso* form from the *d*, *l*-isomers utilizing differences in solubility. X-ray analyses (*42*) indicate that for 1,2-dimethyl-1,2-diphenyldiphosphine disulfide, the higher melting compound is the *meso* isomer(X), in contrast to tartaric acid in which the higher melting compound is the racemate. Attempted resolution of the *d*, *l*-isomers (XI, XII) through chromatography on an optically active



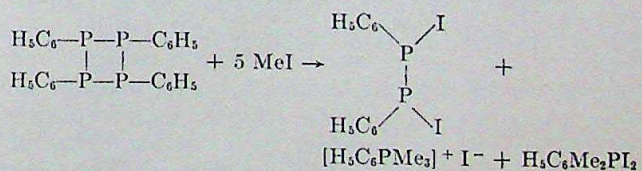
X XI XII

substrate proved unsuccessful (*10*).

Only one report has appeared dealing with optically active diphosphines (*41*). Reduction of asymmetric disulfides results in a mixture of two isomers as shown by NMR spectra. The two peaks presumably represent the *meso* isomer and the *d*, *l*-isomers, the latter pair not being differentiated by NMR. Reduction of either the *meso* or racemate disulfide leads to the same mixture indicating that facile inversion occurs about the tricovalent phosphorus atom. This also explains the failure of attempts to separate the isomers by distillation.

Unsaturated Diphosphorus Compounds, Cyclic Compounds, and Higher Phosphines. Michaelis, in his pioneer work on organophosphorus compounds, obtained a product from the reaction of phenyldichlorphosphine with phenylphosphine which had an empirical formula of C_6H_5P and which he called "phosphobenzol" (*43*). Early workers considered the compound to be formed through the elimination of two moles of hydrogen chloride with formation of an unsaturated diphosphine, $H_5C_6P=PC_6H_5$. More recently, Weil and co-workers (*44*) reinvestigated the synthesis and obtained a compound melting at 193°C compared with 150°C for that of Michaelis. As a result of this discrepancy, they assumed their product to have a greater purity. Reesor and Wright (*45*) repeated the work of Weil and co-workers and decided on the basis of their molecular weight experiments that the compound melting at 154–156°C was the dimer ($H_5C_6P=PC_6H_5$), and the compound melting at 193°C was a tetramer. At the same time, Kuchen and Buchwald (*46*) came to almost exactly the opposite conclusion. They identified the material melting at 150°C as the cyclic tetramer. Strangely, both groups seem to agree on the infrared spectrum of the compounds which they believe to be the tetramer. The results are listed in Table 1. Although Kuchen and Buchwald's molecular weight data are the more convincing, undoubtedly the last word has not as yet been said on these compounds.

Hoffman and Grünewald (*47*) recently investigated the chemistry of "phosphobenzene." They accepted the tetrameric structure and postulated all of their reactions in terms of it. They found that alkyl halides readily split the ring, first giving halodiphosphines, and upon further reaction yielding phosphine derivatives. It should be pointed out that their work does not eliminate an unsaturated diphosphine structure for phosphobenzene:



$[H_5C_6PMe_3]^+I^- + H_5C_6Me_2PI_2$

Table 1. Experimental Data on "Phosphobenzene."

Assigned structure	MW (calc)	Weil		Reesor and Wright			Kuchen and Buchwald		
		mp (°C)	MW	mp (°C)	MW	IR peaks (μ)	mp (°C)	MW	IR peaks (μ)
$H_5C_6P=PC_6H_5$	216	193	198[a]	154–6	206[b]	13.4, 13.5	...	...	...
$(H_5C_6P)_4$	432	...	...	193	402[b]	14.3, 14.4 13.45, 14.32	150.5	410–470[c]	13.5, 14.3
$(H_5C_6P)_x$	...	...	...	252–6	...	...	...	...	...

[a] Determined by Rast method in camphor, ca. 180°C.
[b] Determined isopiestically in carbon disulfide.
[c] Determined cryoscopically and ebullioscopically in benzene, naphthalene, benzil, phenanthrene, and stilbene; all temperatures less than 125°C. Average value of fourteen determinations was 439 ± 23.

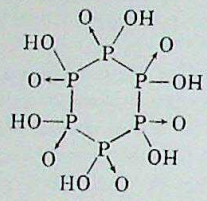
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$$2\ H_5C_6{-}P{=}P{-}C_6H_5 + 5\ MeI \rightarrow H_5C_6PPIC_6H_5^+ + [H_5C_6PMe_3]^+I^- + H_5C_6MePI_2$$

It seems probable however, that the tetrameric structure is the correct one. In contrast to carbon compounds, the four-membered ring appears to be the most stable in the cyclophosphines. Examples of other cyclotetraphosphines are the tetraethyl- (*48*a), tetrabutyl- (*48*b) tetracyclohexyl- (*49*), and *tetrakis*(trifluoromethyl)- (*50*) substituted compounds. The existence of simple double-bonded diphosphorus compounds has never been adequately demonstrated. Compounds previously formulated as unsaturated diphosphorus compounds probably contain four, five, or six-membered rings.

In addition to the organic cyclophosphines described above, a cyclic phosphorus acid consisting of a six-membered ring of phosphorus atoms has been prepared by oxidation of red phosphorus with hypohalites (*51*):



XIII

A few compounds are known containing three linearly connected phosphorus atoms, such as triphosphine (*52*), pentaphenyltriphosphine (*9*), *pentakis*(dimethylamino)triphosphine (*34*), and 1,2,3-*tris*(trifluoromethyl)triphosphine (*53*). In general, these compounds have been but little studied, and some are merely postulated on the basis of a few data.

Reactions Producing P—P Bonds. The most obvious materials suggesting themselves for use in the synthesis of compounds containing a P—P bond are compounds which already contain such a bond. This method is limited in scope inasmuch as the number of compounds available as starting materials is small and there are few reactions available which will alter the molecule without rupturing the P—P bond. Typical of such reactions would be the oxidation of diphosphines with oxygen and sulfur as mentioned above.

A more important synthetic method in the preparation of diphosphorus compounds is the use of white or red phosphorus. Hypophosphoric acid can be prepared in this manner by the oxidation either of red phosphorus by sodium chlorite (*54*) or of white phosphorus by copper nitrate (*55*). Similarly, diphosphorus tetraiodide can be prepared by oxidation either of white phosphorus (*22*) or of red phosphorus (*23*) with stoichiometric quantities of iodine.

A recent study of reactions of white phosphorus with nucleophiles has shown that the reaction proceeds with stepwise cleavage of the cage structure yielding tetracyclophosphines, tetraphosphoric acid, triphosphoric acid, diphosphoric acid, and monophosphoric acid derivatives in various oxidation states. In addition, phosphines and phosphine oxides are produced. The reaction is quite similar to the action of aqueous bases on white phosphorus which gives phosphine, hypophosphite, and phosphite as products (*48*b).

The use of metals to effect the linkage of two halogen-bearing phosphorus atoms appears to be a general and useful method of synthesis. Examples of reactions of this type employing sodium are the preparation of diphosphate(II, II) esters (*32*) and amides (*34*), hypophosphate esters (*39*), and diphosphines (*56*, *57*). The method appears to be applicable to the synthesis of any diphosphorus compound, R_2PPR_2 or $R_2P(O)P(O)R_2$, that does not have a functional group which is attacked by sodium. A reaction which is somewhat similar is the one between diphenylphosphine and diphenylchlorophosphine with elimination of hydrogen chloride (*8*, *9*). Unfortunately this reaction does not appear to have wide applicability and has been used but little.

One of the most interesting reactions resulting in the formation of P—P bonds is that first published by Kabachnik and Shepeleva (*58*). It has long been known that the reaction of Grignard reagents with phosphoryl chloride leads to phosphine oxides or substituted chlorophosphates(I or III) depending on the mole ratio used (*59*). Using a similar reaction Strecker and Grossman (*60*) prepared triphenylphosphine sulfide and tribenzylphosphine sulfide from thiophosphoryl chloride. Kabachnik and Shepeleva found, however, that the reaction of methylmagnesium iodide with thiophosphoryl chloride did not lead to trimethylphosphine, but to tetramethyldiphosphine disulfide. No further work was done with the reaction for a period of about ten years, at which time several papers appeared extending the reaction to ethyl-, *n*-propyl-, *n*-butyl-, and *i*-butyldiphosphine disulfides (*61*–*64*).

No explanation has been given for the difference in reaction product between the phenyl and benzyl Grignard on the one hand and the simple aliphatic compounds on the other. Electronic effects apparently are not responsible since both benzyl and phenyl follow the same path. The significant factor may be a steric effect, for the isopropyl and sec-butyl derivatives could not be isolated (*61*). Perhaps both steric and electronic effects play a part together with a third factor—the solubility of the products—for in no case are the yields high, and other products are always present (*61*). In fact Maier has isolated both the diphosphine disulfide and the phosphine sulfide from such a reaction mixture (*10*).

The remaining methods of producing P—P bonds are mainly of interest because of their intrinsic properties rather than as potentially valuable synthetic routes. An interesting reaction of this type is one involving the formation of tetramethyldiphosphine from an aminophosphine (*vide supra*). The displacement of the dimethylamino group by a dimethylphosphino group apparently is due to some pi-bonding between phosphorus atoms in the product, since basicity and electronegativity arguments, if significant, would tend to favor the P—N compound.

Although the P—P bond is sensitive to oxidation, a compound containing it can sometimes be produced by oxidation of phosphorus in a lower oxidation state if stoichiometric amounts of oxidant are used. Hofmann (*20*) prepared diphosphorus tetraiodide from iodine and phosphine. Brown (*65*) found that very pure diphosphorus tetraiodide could be prepared by oxidation of phosphonium iodide with iodine.

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Probably the most subtle method for effecting P—P bond formation consists of treatment of phenyldiiodophensphine with ether. Iodine splits off with formation of 1,2-diphenyl-1,2-diiododiphosphine (*66*).

Reactions Destroying P—P Bonds. Phosphorus-phosphorus bonds are generally rather susceptible to oxidative cleavage. For example, diphosphorus tetraiodide reacts rapidly with iodine to form the triiodide (*22, 67*). In a similar manner, treatment of substituted diphosphines with bromine or iodine produces the corresponding halophosphines (*9, 56, 68*). Oxidation of diphosphines with oxygen or sulfur yields the chalcogenides, but nitric acid converts the diphosphines to phosphoric (I) acids (*9*) and the diphosphine disulfides to thiophosphoric(I) acids (*69*). Hypophosphate esters also are resistant to atmospheric oxygen and are converted quantitatively to phosphoric(V) acid only with sodium peroxide (*39*).

Tetraaryl- and tetraalkyldiphosphine disulfides are cleaved readily by lithium aluminum hydride to the corresponding disubstituted phosphines (*62*). This reaction cannot proceed through stepwise formation of the diphosphines and subsequent cleavage, since the latter are not cleaved by lithium aluminum hydride. They form adducts from which they can be recovered unchanged (*62*). Both the diphosphines and the diphosphine disulfides are readily cleaved with sodium (*70*).

Burg (*11*) has pointed out that the P—P bond is similar in some respects to the X—X bond in halogens. For example, tetraalkyldiphosphines react with ethylene to form 1,2-*bis*(dialkylphosphino)ethanes:

$$R_2PPR_2 + CH_2{=}CH_2 \rightarrow R_2PCH_2CH_2PR_2$$

An improved synthesis of this class of compounds involves addition of ethylene to the less volatile diphosphine disulfides and subsequent reduction with tributylphosphine (*71*). This type of reaction has not been explored extensively, but should it prove to be of wide scope, it could be valuable in the syntheses of $R_2P—Y—PR_2$ compounds where Y is an unsaturated group.

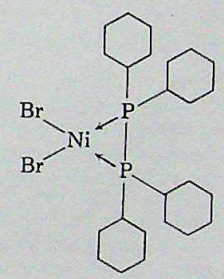
In general, diphosphorus compounds are susceptible to base cleavage. Emeléus and co-workers (*72*) showed that *tetrakis*(trifluoromethyl)diphosphine hydrolyzes in basic solution with complete cleavage of the P—P bond. Less drastic conditions lead to similar results. For example, *t*-butyl alcohol reacts quantitatively with *tetrakis*(trifluoromethyl)diphosphine to form *bis*(trifluoromethyl)phosphine and O-butyl*bis*(trifluoromethyl)phosphate(—I) (*73*). Even as weak a base as trimethylphosphine appears to attack the acidic phosphorus atom, resulting in a weakening of the P—P bond in the molecule attacked. Thus when *tetrakis*(trifluoromethyl)diphosphine is treated with trimethylphosphine and the resulting product allowed to react with dry hydrogen chloride, *bis*(trifluoromethyl)phosphine is produced. Since the original diphosphine is unaffected by dry hydrogen chloride, it appears that coordination by trimethylphosphine has led to an increase in electron density on the phosphorus atom making it more susceptible to attack by the positive hydrogen in hydrogen chloride (*14*). Another example of basic attack is the disproportionation of biphosphine in liquid ammonia (*6*). These disproportionation reactions involving bases may be formally correlated with the disproportionation of halogens under similar conditions and present another example of the pseudohalogen behavior of P—P bonds.

Diphosphorus Compounds as Ligands. Diphosphines are potentially bidentate ligands, but steric effects would appear to be unfavorable for chelate ring formation. Typical examples of diphosphines acting as Lewis bases are the borane and boron trifluoride adducts (*2, 5*), and the nickel carbonyl complex (*74*):

$$(CO)_3Ni—\underset{CF_3}{\overset{CF_3}{P}} - \underset{CF_3}{\overset{CF_3}{P}} - Ni(CO)_3$$

XIV

Likewise, tetraphenyldiphosphine appears to act as a monodentate ligand with respect to transition metal ions such as Cu^+, Ni^{++}, Pd^{++}, and Co^{++} (*75*). On the other hand, the evidence indicates that tetracyclohexyldiphosphine forms three-membered chelate rings with typical transition metal ions (*76*). Three-membered chelate rings are quite remarkable compared with the usually more stable five-and six-membered rings. The rings are probably not strain-free, but they are sufficiently unstrained to be capable of existence, and this fact should be compared with the stability of four-membered cyclophosphine rings. Both stand in sharp contrast to corresponding compounds involving lighter elements.



XV

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Second Summer Inorganic Program at Reed College

An eight week summer program similar to that held in 1962 will be operated again by Reed College, Portland, Oregon, June 17–August 9, 1963. It will present an upper level course in modern inorganic chemistry. Ten college teachers and 20 chemistry majors, who will be seniors in 1963–4, will be chosen as participants. Student stipends of $600 will be made to cover travel and living expenses; teacher participant stipends will be higher.

Lecturers include Professors Gilles, Lipscomb, Hawthorne, MacDiarmid, Dahl, Busch, Seyferth, Gray, Ward, Cunningham, Bartlett, Burg, and Basolo. Laboratory work will be directed by Professor Shore from Ohio State.

Applications should be sent to the Director, Professor Frederick D. Tabbutt, Portland 2, Oregon, by April 1, 1963.

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Proceedings of the California Association of Chemistry Teachers
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Herbert D. Kaesz
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Organometallic Derivatives of the Transition Elements

One of the most exciting developments in chemistry in recent years has been the syntheses of the unusual organo-derivatives of transition metals such as ferrocene, $(C_5H_5)_2Fe$ (I). It was discovered that the metal was equivalently bonded to five carbon atoms of each of the ligands. Following this revolutionary disclosure there has been a great surge both of synthetic and theoretical activity in the field of organometallic[1] derivatives of transition elements with the result that of all the atoms known to bond to transition metals, carbon is proving to be the most versatile. This is all the more striking when one considers that until recently, except for certain complexes like the carbonyls or the cyanides, organometallic derivatives of transition elements were all but unknown. The renaissance of interest in them has had a far reaching effect on our ideas of the nature of the chemical bond, and they have also played an important role in industry.



I

Discovered simultaneously in 1951 by two groups of workers Kealy and Pauson (*33*) from the reaction of cyclopentadienylmagnesium bromide and ferric chloride, and by Miller, Tebboth, and Tremaine (*38*) from the direct reaction of cyclopentadiene with iron at 300°C.

Types of Bonds between Transition Metals and Carbon Atoms

A transition metal may be bonded to a carbon atom of a ligand through a single electron-pair bond, or through a link with multiple bond character. In the former, the bond is formed in the normal way, by pairing two orbitals, one from each atom. The bonding electron pair may be formed from one electron from each atom, or be donated entirely by the ligand into an empty orbital of the metal. Such a bond is also called a σ-bond, in the molecular orbital (M.O.) terminology, because the electron pair is localized on the bond axis. A more detailed description of the M.O. and V.B. theories is given by Coulson (*12*), chapters IV and V, and a comparison of these theories is made in chapter VI. Because these two have been used interchangeably in the field of organometallics thus far, it will be necessary to alternate between them in this review.

For ligands in which the carbon atom is hybridized other than sp^3, an sp^2 or sp hybrid is used for the σ-bond. In addition to this, the unhybridized carbon p orbitals have the proper symmetry and spatial distribution to overlap with unhybridized metal d-orbitals, see Figure 1, as in the carbonyl, cyanide, isocyanide, acetylide, and aryl groups. In M.O. language, the additional overlap is termed a π-bond, in which the ligand makes use of the π^* orbitals, see Figure 1, localized above and below the plane of the metal-carbon bond, with a node (zero-electron density) on the bond axis. The *bond order* in metal-carbon bonds in which double (or $\pi-$) bonding is possible, is usually higher than one, but rarely if ever attains the full value of two. In the V.B. picture, a fractional bond-order is obtained through resonance between various canonical structures, as for instance in the metal carbonyls:

$$\overset{\delta-}{M}\leftarrow C\rightleftarrows \overset{\delta+}{O}: \longleftrightarrow M=C=\ddot{O}:$$

In transition metal complexes, the π-component of the metal-carbon bond plays an important role. In the broadest of terms, it can be described simply as a mechanism for withdrawing electronic charge from the metal orbitals into bonding regions between the ligand and metal. This serves to strengthen the metal-ligand

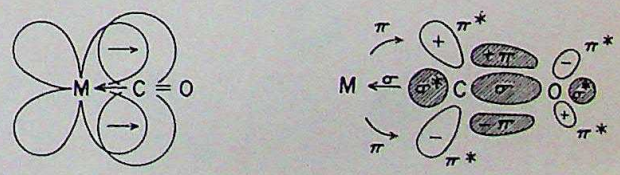


Figure 1. Two possible representations of multiple bonding between metal and carbon of suitable ligand.

Lecture presented at the 4th Annual CACT Summer Conference, Asilomar, California, August, 1962.

I would like to thank Maryellen Rienecke for preparing all of the illustrations, except for Fig. 2 and Fig. 4, which were reproduced by special permission of the publishers of the original work in which they have appeared.

[1] In its most generally accepted definition, the term organometallic is reserved for compounds containing metal to carbon bonds, forming a special class in the broader group of metal-organic compounds. A general review of organometallic compounds both of main group and transition elements will appear shortly in *Scientific American*, see Stone (*50*).

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bond, and otherwise adds to the stability of the entire molecule (see below). The alkyl group is not capable of engaging in any significant multiple bonding with the metal, and it is also observed that simple alkyl derivatives are the least stable of all organometallic compounds of the transition elements. The alkyls, (and many aryls and acetylides) are generally susceptible to moisture and oxygen, and are often thermally unstable (some acetylides are explosive). In ligands capable of π-bonding, an electronegative atom such as either oxygen or nitrogen must be bonded to the metal-bonded carbon atom, in order to facilitate the withdrawal of charge from the metal back into the ligand (as in the carbonyls, cyanides or isocyanides). This bonding is not as easily accommodated, apparently, on such hydrocarbon groups as the acetylides and the aryls.

A metal may be attached simultaneously to *several* carbon atoms of a ligand, and this too has been subjected to theoretical analysis. Two examples might be mentioned here; the bonding of the metal with either ethylene, or a cyclopentadienyl ring. In the former, an M.O. picture has been most widely used, incorporating the familiar concept of electron-pair donation and back-accepting by the ligand. This is the Dewar model (*18*) first proposed for silver-olefin complexes, and most widely applied to olefin complexes of platinum by Chatt and his co-workers (see Fig. 2). The ligand is described in terms of molecular orbitals, and these are combined with suitable orbitals (or hybrid-orbitals) of the metal. The ligand donates the electron pair of its π M.O. into a suitable empty hybrid orbital of the metal. Excess negative charge on the metal may then flow back into the metal-ligand bonding regions, by overlap of suitable filled orbitals of the metal with the anti-bonding (π^*) orbitals of the ligands.

The bond between the cyclopentadienyl ring and the metal has also been extensively studied. A V.B. treatment is presented by Pauling (*42*), (*cf.* p. 385). There are 513 canonical V.B. structures which contribute to the resonance hybrid of the molecule. An alternative description of the bonding is offered by the M.O. treatment of Craig, *et al.* (*12a*). The ligand molecular orbitals are shown in Figure 3*a*. The five $2p$ atomic orbitals of the carbon atoms are combined in various ways to give five M.O.'s for the ring. One of these M.O.'s is singly occupied (one of the π orbitals) and it has suitable symmetry and spatial distribution to overlap with ether the d_{xz} or d_{yz} orbital of the metal (when the principal axis of the metallocene molecule is taken as the z-axis, see Fig. 3*b*). In this picture, then, the bond between the metal and each ring is taken to be composed of an electron-pair, formed by the overlap of the singly occupied π-M.O. of each ring with the suitable singly occupied d-orbital of the metal (the d_{xz} for one ring, and the d_{yz} for the other). Electron-pair metal-ring bonding is also arrived at in the Moffitt M.O. treatment (*39*) in which article an elegant and illuminating explanation is given on the use of symmetry arguments to facilitate such an analysis. The M.O.'s of a number of cyclic polyenes which are able to bond to transition metals, have been presented by Orgel.[2]

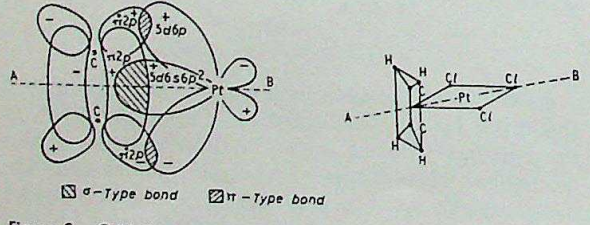


Figure 2. Orbitals used and spatial arrangement of atoms in the combination of ethylene with platinum in $(C_2H_3)PtCl_4^-$; after Chatt and Duncanson, (*6*).

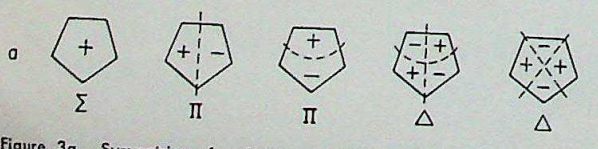


Figure 3*a*. Symmetries of molecular orbitals derived from atomic p_π orbitals.

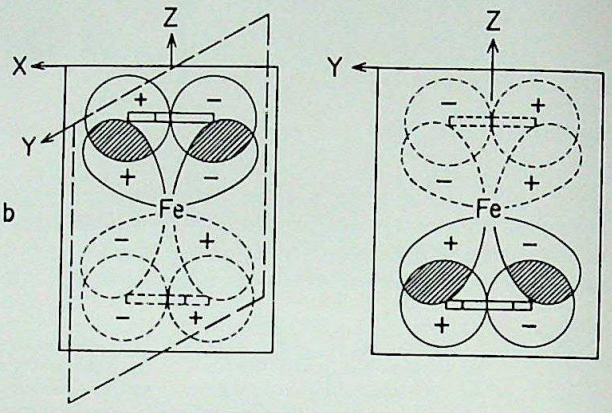


Figure 3*b*. Electron-pair bond from overlap of singly occupied π-M.O. of each ring with singly occupied d_{xz} or d_{yz} metal orbitals; after Craig, *et al*, 1954.

Other M.O. treatments of the metallocenes have been published which postulate greater involvement of ring and metal orbitals. For example, the reader can refer to "Carbon-metal Bonding," J. W. Richardson, in chapter I of Zeiss (*56*), as well as Wilkinson and Cotton (*53a*, p. 85). To follow such discussions it is necessary to be familiar with the applications of group theory to quantum mechanics, as briefly treated by Moffitt (*39*), and also explained in such books as Barrow (*3*).

These have found more or less success in accounting for observed magnetic and spectroscopic properties of these molecules. The main advantage of the m.o. method is that it permits quantitative estimation of such properties, but these are beyond the scope of this review. For a fuller account of the relative merits of valence bond, molecular orbital, and ligand field theories, see Liehr (*34*), in THIS JOURNAL, and also the more recent article by Pauling (*42a*.)

The Sidgwick Effective Atomic Number Rule

In spite of the calculations that have been made so far, there is still a considerable gap between theory and synthetic advances in this field. To present in

[2] See Fig. 10.3.I, p. 155 of ref. (*41a*).

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some orderly fashion the large body of factual information that is now available, it will be necessary to rely on some further simplified generalizations.

The great majority of organometallic derivatives of the transition metals are diamagnetic, and their chemical composition is dictated by the very useful effective atomic number (EAN) rule. This was formulated by N. V. Sidgwick in the 1920's (*48*) before the advent of wave mechanics. Like the *rule of two* (Lewis) or the *rule of eight* (Langmuir-Kossel) the EAN is based on the simple premise that elements will undergo chemical transformations in which, by transfer or by sharing of electrons, they tend to achieve the closed shell configuration of the inert gases. For transition metals, these are the eighteen electrons of the $n\,s$, $n\,p$ and $(n-1)d$ valence orbitals. Each transition metal, in its complexes, tries to add a sufficient number of electrons through coordination (including any that it may have lost through ion formation) to attain this configuration. In modern theoretical treatments (and from the majority of experimental data), it is generally observed that the metal, in its choice of ligand, apparently strives to make profitable use of as many of its valence orbitals as possible. This is held to be,[5] in principle, no more than a restatement of the simple rule of Sidgwick. Since the material presented below constitutes, in my opinion, some very exciting chemistry, one should strive to introduce some of it at any level at which chemistry is taught. At the early stages students will not have been exposed to a sufficient amount of modern valence theory, but it will be seen that no more sophisticated theoretical framework than the Sidgwick EAN rule is really needed under these circumstances. In that case, those few organometallic complexes that are paramagnetic, and/or in other ways do not obey the rule, may be treated separately. In essence, the same difficulties hold for these complexes with respect to the EAN as is true for the paramagnetic molecules such as O_2 or NO, in relation to the octet rule.

One word of caution should be mentioned in connection with the use or the teaching of the EAN rule. If its underlying principle is presented too literally, i.e., that a metal is trying to "*add*" electrons to its valence shell, it would grossly misrepresent the true nature of these elements. It is of course ludicrous to assume that anywhere from six to fifteen electrons may be added to the valence shell of a metal, which is by nature electropositive (electron releasing). It should be stressed that much of this additional charge is not accommodated on orbitals wholly of the metal but in the *internuclear regions between the ligand and metal*. As such, they constitute binding forces the better to attach the ligand to the metal. As some organometallic complexes of the transition metals are unusually stable, this is not a meaningless statement. Therefore, if it is emphasized that the electrons being "added" to the metal to conform to the EAN are in reality *being shared with the ligand atoms(s)*, there is nothing about the qualitative ideas of this rule that violate the basic physics of the bonding in these complexes.

Highlights of Synthetic Developments

σ-bonded Alkyl (or aryl) Derivatives

Alkyl groups are taken to be bonded to the transition metal through a σ-bond. Although an aryl group, such as the phenyl group (C_6H_5) possesses the required features for forming metal-carbon bonds with some π-character, the properties found for the known aryl derivatives of transition metals are such that it is obviously more realistic to discuss them along with the σ-bonded derivatives (the π-character between the phenyl carbon atom and the metal is not very prominent.).

Most of the simple alkyl (or aryl) derivatives, are stable only at reduced temperatures and are also extremely sensitive to air and moisture. Upon warming to room temperature or a little above, they are found to decompose to the free metal and the hydrocarbon radicals. While the discovery of the Grignard reagent (RMgX) in 1900 led to the rapid development of alkyl and aryl derivatives of the main group metals, the treatment of transition metal salts with this reagent led mostly to reduction of the metal and coupling of the hydrocarbon group. The coupling reaction is of interest in its own right (See Cotton (*11*), p. 551). (It was the attempted coupling of two cyclopentadienyl rings which led to the unexpected discovery of ferrocene!) The only really stable simple alkyls of transition metals are the methyl derivatives of platinum (II) to (IV). Tetramethylplatinum (III) exists as a tetramer, as determined by X-ray diffraction in 1947

$$PtCl_4 + CH_3MgI \rightarrow [(CH_3)_3PtI]_4 \text{ mp } 215^\circ \quad \text{(Pope and Peachey, 1909 (44))}$$

II

K in benzene ↙ ↘ CH_3Na

$[(CH_3)_3Pt]_n$ (IV) $\qquad$ $[(CH_3)_4Pt]_4$ (III) (Gilman and Lichtenwalter, 1938 (*22*))

$n = 2$; solution
$n = 12$ or more; crystal

(*47*), see Figure 4. The unusual feature of this molecule is that a methyl group is functioning as a bridging ligand, similar to that found for trimethylaluminum dimer. In the mixed alkylplatinum halide, $(CH_3)_3$-PtI, (II), the halogens are observed in the bridging positions, but this is not suprising as these atoms possess lone pairs which may donate to another metal after a normal covalent bond has been formed to the first metal (*cf.* Al_2Cl_6). The bonding in tetramethylplat-

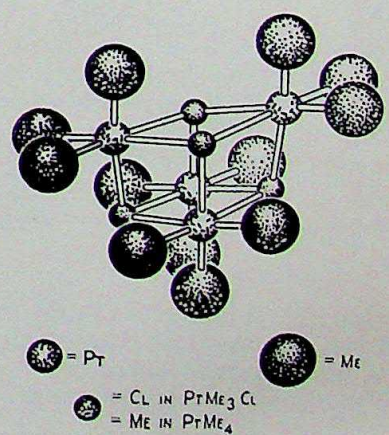


Figure 4. Spatial arrangement of atoms in trimethylplatinum chloride and tetramethylplatinum, after Rundle and Sturdivant, 1947.

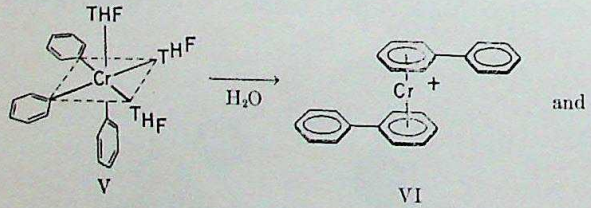
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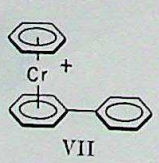
inum tetramer is considered *electron deficient*. A recent review of this topic has been presented by Stone (*49*). The tendency of platinum to engage more than four groups in bonding is observed even at the expense of creating extremely unusual circumstance for a methyl group. It may readily be seen that with ten electrons in the 5*d* and 6*s* orbitals, platinum (in the "*zero-valent*" state) lacks eight electrons to attain the electronic structure of xenon. Covalent bonding to four methyl groups add only four more to the valence shell, leaving the metal "unsaturated." It would then seek additional sources of electron density, which is available through the formation of methyl bridges.

Very few simple alkyl derivatives have been formed for other transition metals.[3] In these derivatives the metal is often coordinatively unsaturated, and they often strongly retain Lewis base solvent molecules (such as tetrahydrofuran, THF, as in $(C_6H_5)_3Cr\cdot(THF)_3$, (V). When the solvent is pumped off, even at low temperature, complete breakdown of the alkyl (or aryl) to metal bonds occurs. These derivatives also tend to add additional carbanion groups (R^- or Ar^-) to form anionic complexes. These are isolated as double salts, such as $LiMn(CH_3)_3$ or $Li_3Cr(C_6H_5)_6\cdot 2.5\ Et_2O$.

Some simple alkyl or aryl derivatives have been reported for Ti, Cr, Mn, Pt, Cu, Ag, Au. Those that are known almost always *do not* satisfy the EAN rule for the metal. Often they are paramagnetic, which may be taken in a rudimentary way, as evidence that not all the degenerate *d* orbitals of the metal have been engaged in bonding. The fact that the EAN rule is not obeyed relates to their general instability, as discussed below. On the other hand, because of this, these compounds are exceedingly useful reaction intermediates. It will be sufficient to mention one or two examples. In the first place, hydrolysis of the tetrahydrofuran complex of triphenylchromium, (V), leads to interesting π-complexes (VI and VII) in which the metal is equivalently bonded to six carbon atoms of the ligand. These proved to be the compounds that were originally thought to be the phenyl derivatives of chromium (*58*), see also the synthesis of dibenzene chromium (*21*).



V VI and



VII

The complex, (V), is also active in the polymerization of acetylene. Some of the possible intermediates and some of the products obtained, are presented in Figure 5. This is similar to the activity of the complexes of nickel, which are generally referred to as Reppe catalysts.[4] This general field is of great interest to the petroleum industry where low molecular weight by-products of the refining process, such as ethylene, propylene, and acetylene are rendered more valuable when converted into polymeric materials.

The instability of simple alkyl (and aryl) derivatives of transition metals has received theoretical interpretation through a quantum mechanical calculation by Jaffe and Doak (*30*). These authors believe that the normal sigma bonds from sp^3 orbital of carbon atom to suitable orbital on a transition metal are weaker than those to main group metals because they have (1) approximately only a third of the ionic resonance energy which makes for stable bonds to alkali and alkaline earth metals and (2) about half the covalent energy (involving terms of overlap integral and ionization potential of the bonded atoms) that make for stable bonds to all the other main group elements. The aryls of transition metals are somewhat more stable than the corresponding alkyls; the bonding orbital of the carbon of the phenyl group contains more *s*-character (sp^2, $33^1/_3\%s$) compared to that in the alkyl group (sp^3, $25\%s$) and this will affect in a favorable direction the ionization potential, overlap integral, and the ionic resonance energy of the carbon metal σ-bond. A carbon sp^2 orbital is more electronegative than sp^3 (See Coulson (*12*), p. 218).

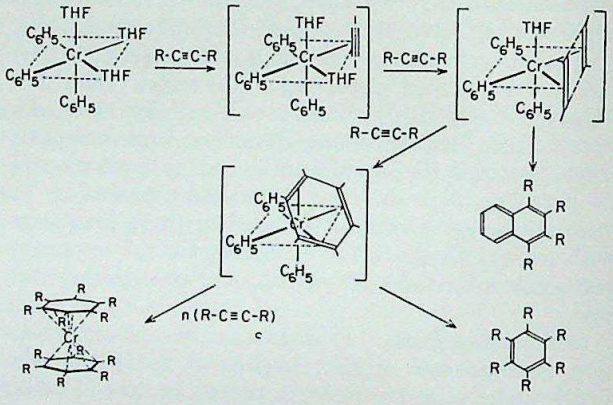


Figure 5. Possible intermediates and isolable products in the polymerization of acetylenes by triphenylchromium tris-tetrahydrofuranate, after Zeiss (56).

In the period following the Jaffe and Doak article, a host of derivatives containing stable alkyl and aryl groups σ-bonded to transition metals have been synthesized such as (VIII) through (XIII). The outstanding feature of these is that due to the presence of other ligands in addition to the σ-bonded groups, the metal appears in the final compound to have attained the electronic structure of the next inert gas. (The σ-bonded alkyl groups count as one, the carbonyls or phosphines as two, and the neutral cyclopentadienyl ring as five electron donors, all counting the metal in the "zero-valent" state, see below.)

It would appear that the transition metal must be "conditioned"[5] to form stable metal-to-carbon σ-bonds.

[3] For a comprehensive review, see "Transition Metal Alkyls and Aryls," G. E. Coates and F. Glockling, chap. 9, Zeiss (*56*).

[4] See "Arene Complexes of Transition Metals," by H. Zeiss, chap. 8, Zeiss (*56*); also, Schrauzer and Eichler (*47a*) and Zeiss (*57*).

[5] See Chatt and Shaw (*7*), or the review by Coates and Glockling, chap. 9 in Zeiss (*56*).

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This conditioning often consists of surrounding the metal atom with sufficient ligands for it to achieve its EAN. From the theoretical standpoint, these additional ligands would be expected to alter the nature of the metal orbital(s) engaged in σ-bonding from those which are used in the simple alkyl or aryl derivative. In M.O. language, the effect of these ligands would be essentially to increase the energy difference between the bonding orbitals, on the one hand, and the non-bonding and anti-bonding orbitals on the other. This would make the latter regions of space less accessible to the valence electrons.

The gain in stability of the complex whenever the metal has attained its EAN can also be interpreted through a kinetic effect. Un-interacted low lying orbitals (either empty or partially filled) would tend to make the derivative in which these are found more susceptible to chemical attack. Such a species would be more easily converted to any other accessible set of products thermodynamically more stable. On the other hand, complexes in which all the low-lying orbitals have been engaged in bonding would present a significant barrier to further chemical conversion, their stability being determined kinetically rather than thermodynamically.[6] The operation of a kinetic-stabiliza-

[6] See also the explanation for the resistance to hydrolysis of SF_6, compared to SeF_6 or TeF_6, as can be found in tests such as Gould (*23*), p. 300.

$(C_5H_5)_2TiCl_2 + 2CH_3Li \rightarrow$ VIII

$(C_5H_5)Mo(CO)_3^-, Na^+ + C_2H_5I \rightarrow$ IX

$HMn(CO)_5 + CH_2N_2 \rightarrow$ X

$Co(CO)_4^-, Na^+ + RCCl \rightarrow RCCo(CO)_4$ XIa

$+CO \rightleftarrows -CO$

$RCo(CO)_4$ XIb

$HCo(CO)_4 +$ → $CH_2{=}CH{-}CH(CO)_4Co{-}CH_3$ XII

$[C_2H_4(PR_2)_2]PtCl_2 + CH_3MgBr \rightarrow$ XIII

tion is illustrated by the evidence for the unusual benzylpentaquochromium ion, $C_6H_5CH_2Cr(OH_2)_5^{++}$ This is found to have a half-life of 1.5 days in aqueous solution, in the absence of air (*1*). It is formed in the reduction of benzyl chloride by chromous perchlorate in dilute perchloric acid solution, and owes its stability to the non-labile character of chromic complexes.

In general, it is not possible to surround a transition metal with a sufficient number of alkyl or aryl groups to achieve the stabilizing effect obtained by use of other types of ligands. In the first place, the σ-bonded groups are only one-electron donors (considering the metal in the "zero-valent" state). Since the transition metals lack anywhere from eight to fifteen electrons to attain their EAN, it would in most cases be sterically impossible to achieve this goal solely with σ-bonded groups. In addition the failure of the σ-bonded groups to engage in π-bonding, i.e., to relieve the metal of negative charge, also contributes to the instability of such derivatives.

Two important recent developments involving σ-bonded alkyl derivatives should be mentioned. Within the last two years, perfluoroalkyl derivatives of transition metals have been synthesized, (*8*) and they appear to be more "stable" than their hydrocarbon analogues.[7] Often, fluorocarbon derivatives are known where the hydrocarbon analogues have not been available i.e., XIV, XV, and XVI. In the perfluorocarbon

$Fe(CO)_5 + C_2F_5I \rightarrow$ XIV

$Fe(CO)_4^-, 2Na^+ + 2R_FCOCl \rightarrow$ XV

$[C_2H_4(PR_2)_2]Ni(CO)_2 + 2CF_2{=}CF_2 \rightarrow$ XVI

group, the strong electron withdrawing properties of the F-atoms acting through the C—F bonds serve to increase the electronegativity of the carbon atom bonded to the metal, which in turn will affect the "stability"of the derivative in question (see above).

Lastly, the unusual reactivity of the alkyl-metal carbonyls, particularly those of cobalt, deserve special

[7] The term "stability" as used here, refers mainly to qualitative chemical observations, such as thermal stability, or resistance to oxygen and moisture. Such usage is known to offend the sensibilities of certain chemists, and perhaps the term "chemical robustness" should be used instead, as suggested recently by Prof. G. E. Coates (during discussions arising at the Symposium on Organometallic Compounds, University of British Columbia, Vancouver, B. C., Sept. 1962).

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mention. The carbonyls and the hydrocarbonyls of cobalt have long been known to display catalytic properties in two well known organic reactions, the *"Oxo"* (hydroformylation) reaction, (XVII), and the Fischer-Tropsch synthesis, (XVIII). Both of these involve two novel reactions of alkylcobalt carbonyls. In the first of these, a metal alkyl derivative is formed by

$$RCH{=}CH_2 + CO + H_2 \xrightarrow{Co_2(CO)_8} RCH_2{-}CH_2{-}CHO \quad XVII$$

$$n\ CO + (2n+1)\ H_2 \xrightarrow{Co_2(CO)_8} C_nH_{2n+2} + n\ H_2O \quad XVIII$$

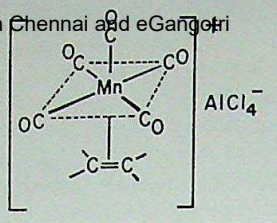
addition of metal-hydrogen of a hydrocarbonyl across the carbon-carbon double bond of an olefin, such as reaction (XII), above. Under pressure (1000 to 6000 p.s.i.) and about 125°C, carbon monoxide may then be inserted between the alkyl group and the metal, such as shown in the reversible reactions (XI*b*) and (XI*a*), above. Depending on the conditions, two routes are possible from this point. In the Oxo-process, hydrogenolysis of the acyl group from the metal gives the aldehyde, (XIX). On the other hand, in the Fischer-Tropsch synthesis, the acyl group is reduced to a new alkyl group containing an additional CH_2 unit, (XX), which can in turn repeat the process (XI*b*) to (XI*a*) and with alternate reduction and carbonylation, lead to higher molecular weight alkanes.

$$RCCo(CO)_4 + H_2 \rightarrow RCH + HCo(CO)_4 \quad XIX$$

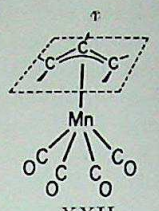
$$RCCo(CO)_4 + 2H_2 \rightarrow RCH_2Co(CO)_4 + H_2O \quad XX$$

(i) CO
(ii) $2H_2$
(repeated many times)

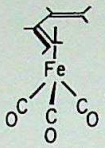
$$\rightarrow R(CH_2)_nCo(CO)_4$$



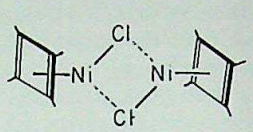
XXI



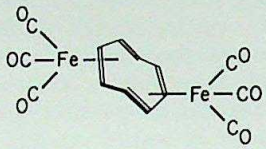
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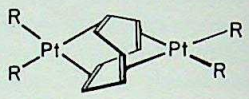
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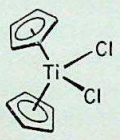
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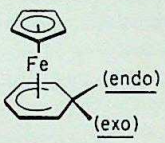
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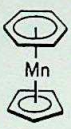
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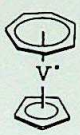
XXVII



XXVIII



XXIX



XXX

Olefin Complexes

It is very likely that the first organometallic derivative of a transition element was the olefin complex discovered in 1827 known as Zeise's salt (*55*), $[CH_2{=}CH_2{\cdot}PtCl_3]^-$, $K^+{\cdot}2H_2O$. Since that time, olefin complexes of other transition metals have been discovered, such as the silver-olefin complexes, and in 1930, the butadiene adduct of iron carbonyl, C_4H_6-$Fe(CO)_3$, Reihlen, Gruhl, Hessling, and Pfrengle (*46*). A comprehensive review of olefin compounds has been given by Fischer (*20*) or Zeiss (*56*). After the discovery of ferrocene in the early 1950's, complexes of olefins and transition metals have been synthesized in great profusion. It is now clear that a transition metal can be attached to an olefin by engaging simultaneously anywhere from two to seven of its carbon atoms in bonding. A sample of some of the known complexes is given in structures (XXI) through (XXX), as well as in some of the other structures presented in this article. To determine whether the metal has achieved its EAN in any of these, any one of a number of alternative schemes may be followed. In the neutral complexes, it is convenient to consider the metal in the "zero-valent" state, and the ligand as a neutral olefin or radical. A ligand attached to a metal through *n* carbon atoms may be considered an *n*-electron donor; one singly occupied *p* orbital from each olefinic carbon atom is involved with the metal. It is equally acceptable to regard certain ligands as negatively charged, which must then be balanced by suitable positive charge on the metal, if the complex is neutral. For instance, in the cyclopentadienyl derivatives, a neutral C_5H_5 ring is regarded as a 5-electron donor to a "zero-valent" metal, or as a negatively charged ring, $C_5H_5^-$, donating 6 electrons into a suitably ionized metal atom. Application of the EAN is only a formalism and it can not be stated with certainty which of these two alternative approaches is the more correct one.

Most olefin-metal complexes are diamagnetic and obey the EAN rule. The chemistry of the cyclopentadienyl derivatives has recently been reviewed in THIS JOURNAL (*45*).

The Carbonyls and Mixed Olefin-Metal Carbonyl Complexes

The carbonyls have been recognized as an unusual type of transition metal complex since the discovery of $Ni(CO)_4$ by Mond, Langer, and Quincke in 1890 (*40*). They obey the EAN rule with the sole exception of $V(CO)_6$, which is monomeric and paramagnetic (one unpaired electron).[8] Recently, some substituted carbonyls have been isolated in which the EAN rule is not obeyed, for instance, some phosphine and diarsine

[8] The chemistry of the carbonyls has recently been reviewed in THIS JOURNAL, see PODALL (*43*). For a comprehensive treatment see CHATT, PAUSON AND VENANZI, chap. 10 in ZEISS (*56*).

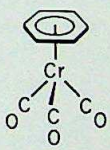
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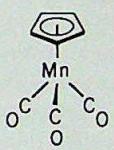
complexes of manganese carbonyl, $C_6H_5Mn(CO)_3$, and $[C_2H_2(AsR_2)_2]Mn(CO)_3$. No simple explanation is yet available why these and some other similar complexes do not exist as dimers, with metal-metal bonds, as does, for instance the parent carbonyl, $Mn_2(CO)_{10}$. Last year, the preparation of $Tc_2(CO)_{10}$, long missing last member of the manganese sub-group carbonyls, was reported (27*a*, 27*b*). Technetium does not occur in nature and is available only through synthetic nuclear processes. It is now being recovered in gram quantities from residues of atomic reactors, and we should be seeing more of its organometallic chemistry reported in the next few years (see below).

Two types of metal-carbon bonding are generally recognized in the carbonyls; the terminal CO group, in which the carbon atom is bonded to one metal, and the bridging group in which the carbon is attached to two metals. In the former, the ligand is taken to donate two electrons to the metal; in the latter, one electron is being donated to each of the two metals. The manner with which these two types of bonding, and also the formation of metal-metal bonds are combined in the known carbonyls to give the EAN for the metal is amply discussed in the references cited above,[8] and also in many standard texts.

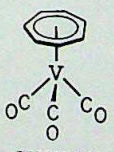
The carbonyls often serve as convenient starting materials for the synthesis of olefin complexes. Many instances are known where mixed olefin-carbonyl derivatives are isolated. In olefins attached to the metal through an even number of carbon atoms, each double bond can displace a carbonyl group, such as in the complex (XXI), above, which may be considered a substitution product of $Mn(CO)_6^+$, $AlCl_4^-$. In the diene-complexes, such as (XXVIII) and (XXV) above, two CO groups in the starting material ($Fe(CO)_5$) have been displaced from each metal atom. In benzene-chromium tricarbonyl, (XXXI), the olefin has replaced three



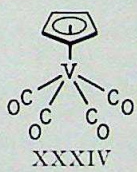
XXXI



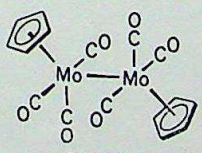
XXXII



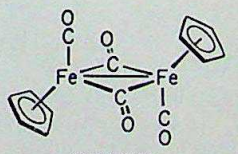
XXXIII



XXXIV



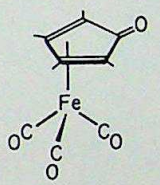
XXXV



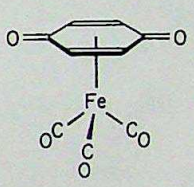
XXXVI

CO groups in $Cr(CO)_6$. Olefins in which an odd number of carbon atoms are bonded to the metal are considered as odd-electron donors. The odd electron must somehow be paired in the final complex, if it is to be diamagnetic and follow the EAN rule, which the great majority do. The odd electron may take the place of the metal-metal bond (if any) in the starting carbonyl, in cyclopentadienyl manganese tricarbonyl (XXXII). In the vanadium complexes, (XXXIII) and (XXXIV), the odd electron of the ligand has paired with the odd electron in the starting carbonyl. For other carbonyls in which no metal-metal bonds were present, the odd electron-donating olefin will displace an even number of CO groups, and then the final complex will contain a metal-metal bond, see (XXXV) and (XXXVI). Alternately, the odd electron in such mixed olefin carbonyl complexes may be used for σ-bonding to an alkyl (or aryl) group, such as in (IX), above.

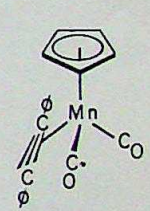
No group of ligands has proved itself more versatile than the acetylenes, and their reactions with metal carbonyls deserves special mention. Similar to the activity of the alkyl-transition-metal derivatives (see Fig. 5 above), the carbonyls have also been found to polymerize acetylene, and here also it was principally through the pioneering work of Reppe and his collaborators. Many new and interesting olefins have been synthesized, containing two, three, or four acetylene units. Often, carbon monoxide is polymerized together with acetylene, and unsaturated cyclic ketones and diketones have been obtained. Some of these may be isolated while still attached to the metal carbonyls, (XXXVII) and (XXXVIII). In rarer cases, the acetylene is found bonded to the metal without having undergone any polymerization, (XXXIX) and (XL). In the



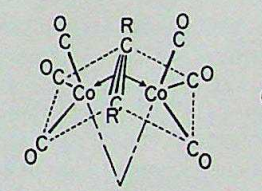
XXXVII

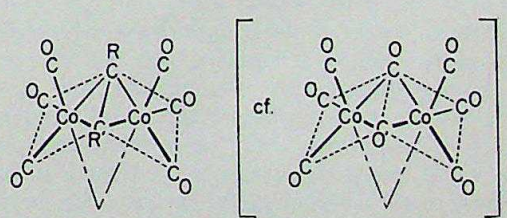


XXXVIII



XXXIX





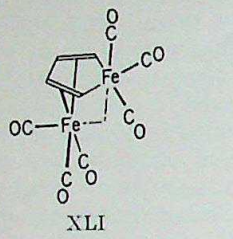
XL

latter, this ligand is demonstrating its ability to π-complex simultaneously to two metals, owing to the two π-bonds at right angles to each other from which the triple bond is composed (see also below). It will be necessary to refer to further sources for more detailed coverage of this field, which by now has grown to vast proportions,[9] but it would not be possible to leave this topic without giving a sample of some of the truly novel structures than have been thus far obtained (see (XLI) through (XLIV)). The adduct $Fe_2(CO)_6 \cdot (RC_2R)_2$, XLI, is isolated from the reaction of acetylene

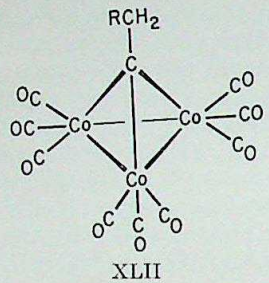
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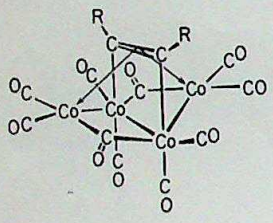
with iron carbonyl,[8,9] but has also been obtained from reaction of thiophene with iron carbonyl (*31*). The cobalt adduct $Co_3(CO)_9 \cdot (RC_2H)H$, (XLII), contains a carbon atom bonded to three cobalt atoms. It can be formed only from mono-substituted acetylenes, as migration of acetylenic hydrogen most likely is involved in its formation (*5*). It is obtained by treatment of the adduct of the type $Co_2(CO)_6 \cdot (RC_2H)$, (XL), with alcoholic HCl (*36*). The mechanism of formation of many of these interesting complexes awaits future studies. It would appear that even greater degrees of complexity are possible, with the two structures (XLIII) and (XLIV), however, some degree of order is beginning to be apparent. In the complex, $Co_4(CO)_{10} \cdot (RC_2R)$, (XLIII), the arrangement of cobalt



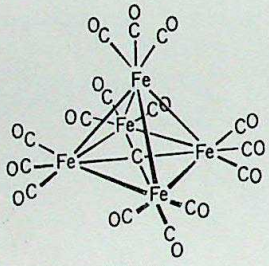
XLI



XLII



XLIII



XLIV

atoms around the acetylenic carbon atoms is found (*15*) to resemble somewhat the arrangement found in thorium dicarbide, in which each C_2 group interacts with six thorium atoms. It is likely then that the even more perplexing structure, (XLIV), might also prove to be analogous to other known types of carbides. The function of the lone carbon atom in $Fe_5(CO)_{15}C$ (*4*), would surely resemble those carbides in which discreet carbon atoms can be recognized (see below). In any case, these complexes are diamagnetic, and it is left to the reader to puzzle whether the metal has achieved its EAN. From these very recent advances, perhaps future work might be predicted. Would it not be of interest to see whether metal carbides can be treated with olefins and/or carbon monoxide, to see whether any other intermediate types of compounds such as (XLIII) and (XLIV) can be obtained?

Cyanides, Isocyanides, Acetylides, and Carbides

These compounds are included in the general topic of organo-derivatives of transition metals because they contain metal-carbon bonds. It is interesting to compare these to the metal-carbon bonds in the alkyl, aryl, carbonyl derivatives and the olefin complexes, as discussed above. No more will be said here, however, than to give leading references where further detailed and up to date information may be found on these.

A recent review of the cyanide complexes of transition metals is available, Griffith (*26*). The CN^- ion is isoelectronic with the CO group. It is also chemically related to the isocyanides through an alkylation reaction, of which typical examples may be:

$$Fe(CN)_6^{4-} + C_2H_5I \rightarrow (C_2H_5N{=}C)Fe(CN)_5^{3-} + I^- \quad \text{XLV}$$

$$Fe(CN)_6^{4-} + (CH_3)_2SO_4 \rightarrow (CH_3N{=}C)_6Fe^{++} + 3\ SO_4^{=} \quad \text{XLVI}$$

Isocyanide complexes of metals have recently been reviewed by Malatesta (*35*).

Complex acetylides of transition metals, containing the ligand $RC{\equiv}C^-$, where R = alkyl, aryl or H, have been reviewed by Nast (*41*). The acetylides containing the group $(C{\equiv}C)^{--}$ are classed with the carbides, of which two main types are recognized; those containing the aforementioned group, and those containing discreet C atoms (or C^{4-} ions). The former yield acetylene upon hydrolysis while compounds of the latter group generally yield methane, see Wells (*52*), p. 760. Perhaps work in the near future will show a closer resemblance of this type of compound to certain metal olefin and/or carbonyl complexes (see above).

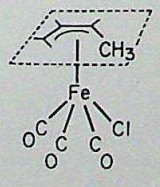
Future Trends

Certain areas of organometallic chemistry of the transition elements are probably going to receive widespread attention in the next few years. Certainly, we can expect more developments in the novel fluorocarbon complexes, only recently discovered (see above). Also the newly discovered relationship between the metal carbides and certain derivatives obtained from the reaction of acetylenes with metal carbonyls (see above) will very likely be investigated further. It will be exciting to follow these developments, and see how they enhance or modify our ideas concerning bonding of carbon and transition metals.

Many other developments in the current literature are so novel that they have not been represented in the typical reactions discussed above. Since the field of organometallic derivatives of the transition elements is undergoing rapid expansion and change, a selected number of such developments are separately mentioned here.

It is known that olefin complexes can be protonated. While in some cases the proton may become attached to the ligand, as in (XLVII) (*29*), in some other complexes, it is almost certainly attached to the metal, (XLVIII) and (XLIX) (*53*). The interesting Lewis-base properties displayed by the metal in the latter two have been theoretically interpreted (*2*). It is apparent

butadieneiron tricarbonyl + HCl →

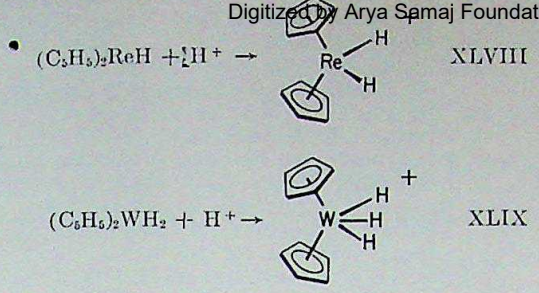


XLVII

[9] See Coates and Glockling in Zeiss (*56*), or Coates (*9*). The developments in this field are so rapid, it is also necessary to read the current literature, principally under the names: W. Hubel, I. Wender, or E. R. H. Jones, and their collaborators. For X-ray diffraction structure studies of novel complexes, see under L. F. Dahl, O. S. Mills, or G. S. D. King, and collaborators.

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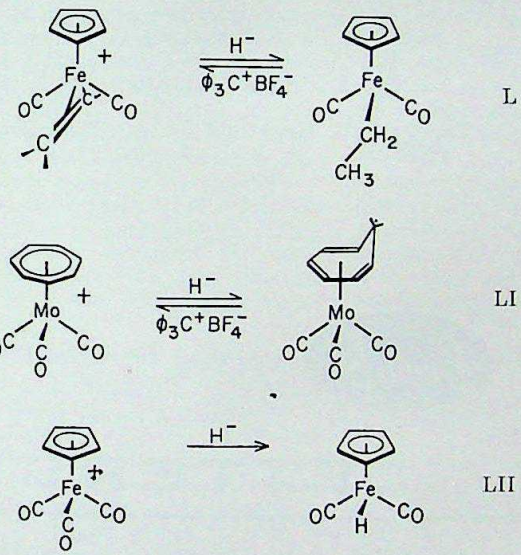
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that the non-bonding electrons of the metal in these metallocenes are available for interaction with additional groups. This could be taken as experimental evidence that not all the metal electrons are engaged in bonding to the C_5-rings, which lends physical reality to the picture of *electron pair* bonding between metal and ring of Craig, *et al.*, or of Moffitt (see above).

Cationic metal complexes may be reduced by hydride ion, and also in this case, it is possible to observe final-attachment of the entering group either on the ligand, (L) (*24*), and (LI) (*16*), or on the metal, (LII) (*17*). The reaction may be reversed by trityl fluoroborate, as shown.

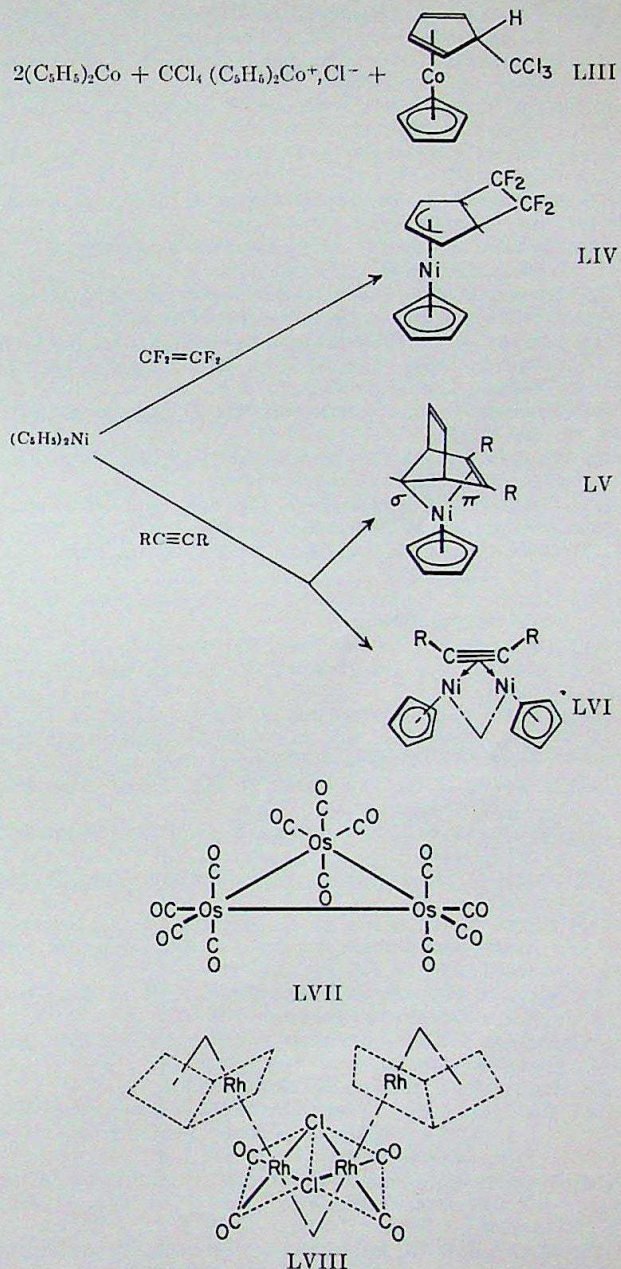
Certain olefin complexes in which the EAN for the metal is being *exceeded* will readily undergo oxidation



or other reactions in which less involvement of electrons (and/or ligand atoms) with the metal are observed. The action of CCl_4 on cobaltocene (*32*) and (*25*) serves to illustrate this principle, (LIII).

Some of the reactions of nickelocene also follow this principle, such as (LIV) (*37*), (LV) (*19*), and (LVI) (*51*). The displacement of an entire C_5H_5 group in the latter reaction is closely related to the action of CO to give $[(C_5H_5)NiCO]_2$.

Lastly, it should be mentioned that we are becoming more aware of metal-metal bonds in organometallic (and other) complexes of transition metals, see compounds (XLI) through (XLIV), as well as some previous derivatives cited in this article. Until about five years ago, it was believed that bonds between transition metals *without other bridging groups*, would not be stable enough to exist in isolatable compounds. The first to be discovered containing a free metal-metal bond, were the cyclopentadienyl tricarbonyls of the chromium sub-group metals (*54*), see (XXXV) above, and the carbonyls of manganese and rhenium (*13*). Many more compounds have been discovered since, with even more novel metal-metal bonding, including the derivatives (LVII) (*10*), (LVIII) (*14*), and the recently reported cyclopentadienyl of technetium $[(C_5H_5)_2Tc]_2$ (*28*). The metal-metal bond in these accounts for their diamagnetism, and also, these obey the EAN rule.



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ChemEd

LETTERS

To the Editor:

In his recent review of my "Elements of Chemical Thermodynamics" (THIS JOURNAL, 40, 51 (1963), Prof. Mahan is too generous in attributing to me the "neat sidestep" of making q "stand for both finite and infinitesimal quantities of heat": I have only followed in the footsteps of Lewis and Randall. He is too generous also in attributing to the slipperiness of this road a fall due to an oversight on my part: the equation he cites will of course read smoothly when one simply introduces the omitted sigma

$$\Delta S = \Sigma q_{rev}/T = \int C_p dT/T$$

LEONARD K. NASH

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BOOK REVIEWS

Valence

C. A. Coulson, University of Oxford, England. 2nd ed. Oxford University Press, Oxford, 1961. ix + 404 pp. Figs. and tables. 14.5 × 22.5 cm. $6.

Approximately ten years have passed since the first edition of this book was printed. The reviewer of that edition (J. CHEM. EDUC., 29, 532 [1952]) pointed out that much of the discussion involved mathematical equations, which for most chemists would require some effort to follow. For the non-mathematically-minded chemist, the same may be said of the second edition.

For the most part, the chapters and their arrangement are the same as in the first edition. However, clarifying alterations appear in numerous instances, e.g., rewording, expansion of discussion, addition of a half-dozen figures, and additional equations to reduce gaps in following the mathematical developments. The chapters on theories of valence, wave-mechanical principles, molecular orbital theory, valence-bond theory, and nonmetallic solids remain virtually unchanged. Slightly greater expansion was made in the chapters on the comparison of molecular orbital and valence-bond theories, polyatomic molecules, conjugated and aromatic molecules, metals, and atomic orbitals. In the last, the change involves an expansion of about two pages on the topic of *d*-orbitals, and the discussion is shifted to the end of that chapter. There has been appreciable rewriting of the chapter on hybridization. The most extensive change has been made in the last chapter, namely, the hydrogen bond and other miscellaneous topics. This chapter, which has been expanded by about 50% in the number of pages, includes such topics as hyperconjugation, hindered rotation around a single bond, electron-deficient molecules, boron hybrides, theoretical interpretation of bridge structure, inorganic π-electron rings (new in the second edition), and mesoionic compounds. It is the opinion of this reviewer that cursory coverage of such complex topics which, in some cases, are still unresolved detracts from the merits of the book. The uninitiated reader may feel he has been exposed to these topics, but he is not likely to feel sufficiently secure to apply this exposure.

The major change in the second edition is the introduction of an entire chapter on ligand-field theory. This chapter is primarily descriptive and a large part of the discussion can be followed by most readers. In certain sections, however, it is likely that the person who has had no prior contact with ligand-field theory will find some difficulty in keeping track of the terminology and in following the discussion involving symmetry considerations.

There are several excellent features of this book, written by a recognized authority in the field. Physical interpretations frequently accompany the mathematical equations, and figures and graphs clarify mathematical aspects which otherwise might be obscure. In brief statements throughout the book, the author cautions the reader about misinterpretation of concepts such as those pertaining to resonance, hybridization, electronegativity, and bond additivity. Many of the concepts, however, are so widely utilized that someone glancing at selected sections and not reading the full text carefully may miss these very important remarks. The reader who is willing to take a little time will gain some acquaintance with the ideas and terminology which are so prevalent in current chemical literature, although in some sections both the ideas and terminology may seem rather strange, e.g., "Li⁻ atoms" and "negatively bicovalent ions" (p. 334).

In addition to the above changes, many numerical values have been brought up to date, as evidenced by the many changes in the discussion and in tables. Two items which apparently slipped by the updating process are the reference (p. 235) to the existence of OsF_8, which recently has been shown to be OsF_6, and the reference (p. 138) to CsF as being the most polar of all molecules, which is not in accord with evidence based on measurement of dipole moment and internuclear distance.

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Reviewed in this Issue

C. A. Coulson, Valence
Philip John Durrant and *Beryl Durrant*, Introduction to Advanced Inorganic Chemistry
A. I. Dahl, editor, Temperature: Its Measurement and Control in Science and Industry. Volume 3, Part 2, Applied Methods and Instruments
H. W. Thompson, editor, Advances in Spectroscopy. Volume 2
E. H. E. Pietsch, editor, Gmelins Handbuch der Anorganischen Chemie, 8. Auflage, System-Nummer 28, Calcium. Part B, Section 3
E. H. E. Pietsch, Gmelins Handbuch der Anorganischen Chemie, 8. Auflage, System-Nummer 52, Chromium. Part A, Section 1
Bernice T. Eiduson, Scientists: Their Psychological World
Chem Sources, 4th ed.
Harold A. Scheraga, Protein Structure
Edward M. Kosower, Molecular Biochemistry
Michael Kasha and *Bernard Pullman*, editors, Horizons in Biochemistry: Albert Szent-Györgyi Dedicatory Volume
F. G. A. Stone, Hydrogen Compounds of the Group IV Elements
Sister Martinette Hagen, Clathrate Inclusion Compounds
Peter Sykes, A Guidebook to Mechanism in Organic Chemistry
William A. Pryor, Mechanism of Sulfur Reactions
Marcel Florkin and *Elmer H. Stotz*, editors, Comprehensive Biochemistry. Volume 2, Organic and Physical Chemistry
E. L. Gefter, Organophosphorus Monomers and Polymers
Russell L. Ackoff in collaboration with S. K. Gupta and J. S. Minas, Scientific Method: Optimizing Applied Research Decisions
Friedrich Klafes, Lehrbuch der Organischen Chemie, Band 2
Norman Kharasch and *Walter Wolf*, compilers and editors, Index to Reviews, Symposia Volumes and Monographs in Organic Chemistry for the Period 1940–1960
H. J. Emeléus and *A. G. Sharpe*, editors, Advances in Inorganic Chemistry and Radiochemistry, Volume 4

Introduction to Advanced Inorganic Chemistry

Philip John Durrant, Cambridge University, and *Beryl Durrant*, University of London. John Wiley and Sons, Inc., New York, 1962. xv + 1171 pp. Figs. and tables. 17 × 25.5 cm. $15.50

The Durrants, an experienced team of textbook writers at the University of Cambridge, have produced a comprehensive inorganic source book which their British publisher Longmans, Green and Company is able to sell at a bargain price in this country ($15.50). The book follows the usual format of theoretical followed by descriptive chemistry and takes its place beside (but dwarfs in size) Moeller, Partington, Heslop and Robinson, Cotton and Wilkinson, etc. Like all the above, except the last, the ratio of pages is such that the transition elements get relatively short shrift.

The only reason for writing another inorganic text is that the authors have a different point of view to present. In this case the Durrants discard the approach based on accessibility and familiarity of compounds in favor of a systematic treatment based on theoretical principles. Questions of whether chemistry is yet ready for this aside, the logical extention of the scheme would be to make the book a catalog of undiscovered compounds. Happily, a masterful compromise is at hand, and a system based on

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modes of hybridization from valence bond theory is used to classify the compounds of each element. Oxidation state is used in the usual way for the transition elements.

The book opens with a sound and advanced treatment of quantum theory and valency. Valence bond and molecular orbital theories are discussed and compared. This is followed by excellent discussions of spectroscopic methods, with summaries of results and information which can be derived from each method. The theoretical section concludes by considering bond lengths, dipole moments, bond energies and the determination of crystal structures. A novel method for calculating bond lengths from other data is presented. This section is longer and on a higher level than each of two theoretical inorganic textbooks recently published in this country.

The descriptive chemistry is presented with the same high level of sophistication. The chemical cliché is carefully avoided and many new and interesting interpretations are offered. Unfortunately, some of these confuse rather than enlighten as when we are told that hydrogen is not a reducing agent or that nitrogen and phosphorus exhibit the same oxidation state in all compounds (especially in light of the subsequent discussion of the oxidation of ammonia and PCl_3). In the transition series, the normal prehybridization electron configurations are given in most cases as including *np'* electrons. No reason is given. Nomenclature is occasionally annoying as with the silanes and it is also annoying to read that lithium, beryllium and boron *atoms* are electron deficient. Other minor points include an incorrect statement of the boiling points of fluoromethanes and a puzzling one to the effect that aromatic compounds with fluorine atoms in the side chain behave as aliphatic. More serious is that HBr is stronger, not weaker than HCl and this argument cannot be used to explain the hydrolysis of metal bromides. The structure of S_4N_4 given in two places with N-N bonds is wrong and in discussing the acceptor properties of boranes, ΔH values are more significant than temperatures of dissociation. It is not true that P and S exert more than four σ bonds only in combination with fluorine. It *is* surprising to read that FeO, Fe_2O_3 and Fe_3O_4 are not chemical compounds (nowhere defined) but not very surprising that monomeric carbonyls are more volatile than others. Finally, typographical errors are to be expected in the first edition of so large a work and a modest number are found (e.g., pp. 383, 467, 590, 262, 648, 663, 681, 772, 813, 896, 961, 1030, and 1084). The lack of references to key points is, however, regrettable.

On the balance, the Durrants have produced an encyclopedic work of great sophistication and originality. The method of classification according to hybridization states of the elements offers great advantage over other classifications based on binary compounds with various elements, oxidation states, or on historical, geological or industrial interest, and is in keeping with the direction of progress in the science. Orbital diagrams of a novel type are used to clarify bonding situations for the reader. It is regretted (but understandable) that kinetics, thermodynamics and nuclear chemistry could not find their place in this volume. The book is already the most comprehensive on the subject since Sidgwick and its unique method of classification makes it an excellent reference volume.

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Temperature: Its Measurement and Control in Science and Industry. Volume 3, Part 2, Applied Methods and Instruments

Edited by *A. I. Dahl*, General Electric Co., Schenectady, New York. *Charles M. Herzfeld*, Bureau of Standards, Washington, D. C., editor-in-chief. Reinhold Publishing Corp., New York, 1962. xiv + 1094 pp. Figs. and tables. 18.5 × 26 cm. $29.50

It is necessary to preface our remarks on the book being reviewed here with the explanation that the proceedings of the Fourth Symposium on Temperature held in 1961 are being published in Volume 3 under a title used for two previous symposia—Temperature, Its Measurement and Control in Science and Industry. The proceedings of the Second Symposium were published in 1941 in Volume 1 and those of the Third Symposium in 1955 in Volume 2. Volume 3 differs from Volumes 1 and 2 in that it will be published in three parts, i.e. three separate books, under the headings: Part 1, Basic Standards, Concepts and Methods; Part 2, Applied Methods and Instruments; and Part 3, Zoology and Medicine.

Part 2, which is being considered here, contains the papers presented at the Fourth Symposium which were grouped under the following section headings: Section I, Thermoelectric Thermometry; Section II, Resistance Thermometry; Section III, Radiation Thermometry; Section IV, Dynamic Temperature Measurements; Section V, Automatic Methods of Temperature and Control; Section VI, Miscellaneous Temperature Methods and Techniques; and Section VII, Temperature Sources and Thermal Imaging Techniques.

The present volume serves the purpose of bringing up to date a number of topics which appeared in Volume 1 but were largely omitted in Volume 2. Hence, in Volume 3 such topics as automatic temperature regulation, radiation pyrometry, thermoelectric thermometry are again covered thoroughly and include the advances achieved in the interim between the Second and Fourth Symposium.

Thermoelectric thermometry remains the most important single topic. This is reflected in the fact that fully one-quarter of the book is devoted to it alone. Papers on the physical properties and application of many new thermocouple materials are included with particular emphasis on the high temperature range. The subject of dynamic and transient temperature measurement under a variety of experimental conditions is thoroughly treated in a number of significant papers. Also, the great progress in automation involving temperature and temperature control is evident if one compares the sections dealing with this subject in Volume 1 published in 1941 and the present Volume 3 published in 1962.

On the whole, the papers are well written and contain many useful tables, graphs and drawings. Most of the papers have complete bibliographies, and therefore will simplify the procedure of obtaining more detailed information on subject matter where desired. Author and subject indices are provided.

In make-up and emphasis the present book resembles Volume 1 of the series much more closely than Volume 2. Needless to say, it will be found to be an extremely useful reference source for any one interested in the practical and engineering aspects of temperature and temperature control.

The one disadvantageous feature appears to be the large size (over 1000 pages, 7 in. × 10 in.) and the correspondingly high cost. When this is combined with the fact that it is only one book of three comprising Volume 3, it can only mean that it will have fewer owners and users than would otherwise be the case. Perhaps the answer lies in minimizing overlap of topics within the various parts of the volume, screening out papers not presenting significantly new subject matter etc. in order to keep the size within manageable limits. Otherwise, the prediction one can make is that the seriousness of the problem of the size of the volumes will increase with future symposia.

E. L. Pace
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Avdances in Spectroscopy. Volume 2

Edited by *H. W. Thompson*, St. John's College, Oxford, England. Interscience Publishers, Inc., 1961. xi + 483 pp. Figs. and tables. $13.

The appearance of the second volume of this "Advances ..." series provides a welcome addition to the chemist's and chemistry teacher's reference shelf. Professor Thompson has kept admirably to his declared aim to provide "authoritative surveys on recent progress in different fields (of spectroscopy) written by experts who themselves contributed to it." The choice of topics and authors is quite timely and appropriate. They include: Application of Atomic Absorption Spectra to Chemical Analysis (A. Walsh); Spectra of Flames (A. G. Gaydon); X-Ray Spectroscopy (Herbert Friedman); Nuclear Magnetic Resonance (R. E. Richards); Infra-Red Spectra of Crystals (W. Vedder and D. F. Hornig); Refraction of Gases in the Infra-Red (J. H. Jaffe); Infra-Red Spectra of Micro-organisms (K. P. Norris); The Ultra-Violet Absorption Spectra of Proteins and Related Compounds; (G. H. Beaven); Some Recent Developments in the Theory of Molecular Energy Levels (H. C. Longuet-Higgins). The authors of the various chapters are indeed contribut-

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ing experts and their articles have been written clearly and accurately. The list of references appended to each is both extensive and representative. In this connection, the volume is oriented more to the teacher who wishes to keep abreast of many fields than it is to even the most sophisticated student. Even for the graduate student, a considerably wide background must be presumed for full appreciation of the various topics. It is expected that this volume, as is true of its predecessor, will find its use as ready reference, first as an up-to-date survey of a particular field, and, second as a beginning point for a more extensive literature search. It is therefore with considerable pleasure that this reviewer noted that theory as well as experimental subjects has been treated extensively. The range and breadth of topics from X-ray to infrared, atomic and molecular spectra, and "pure" theory to such specifics as protein spectra, is refreshing at a time when researcher, teacher and student alike, finds himself almost overwhelmed by the vast volume of published data. A volume such as this fulfills a great need by providing the earnest reader with a single series by which he may conveniently keep up to date with the burgeoning fields of spectroscopy.

Small discomfitures could be found, such as the difficulty in locating a specific topic or the lack of uniformity in referencing (the 20 page bibliography compiled by Vedder and Hornig is probably the most useful to the overall purpose of the series). But such discomfitures are minor compared to the timeliness, authoritativeness, and extensiveness of the work. We look forward to a promised third volume which will "complete a survey of other established fields (of spectroscopy), and. . . include a few of the very recent developments."

Ellis R. Lippincott
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College Park

Gmelins Handbuch der Anorganischen Chemie, 8. Auflage, System-Nummer 28, Calcium. Part B, Section 3

Edited by the Gmelin Institute under the direction of *E. H. E. Pietsch*. Verlag Chemie, GMBH, Weinheim, Bergstrasse, 1961. lxii + 912 pp. Figs. and tables. 18 × 25.5 cm. Cloth bound. $142.

This volume is Part B, Section 3, of the revised Gmelin treatment of calcium. See THIS JOURNAL, 35, A614 (1958). It concludes the discussion of calcium compounds begun in Section 2, and treats those substances composed of calcium and the following: sulfur, selenium, tellurium, boron, silicon, phosphorus, arsenic, and bismuth, and their oxygen-containing compounds. Those treated most extensively are the sulfates, sulfites, carbonates, silicates, and phosphates. In addition, double salts with alkali metal salts are discussed, as are many compounds of calcium with organic substances. A section on detection and determination devotes 76 pages to calcium and 78 pages to strontium and barium.

pounds, but their behavior in water is well covered. The more important substances are treated under the headings of formation, physical properties and chemical properties. Special points are not neglected. Among these the following illustrations are given: luminescence of selected compounds; photoconductivity of gypsum; detection and determination of calcium isotopes.

The Contents pages are arranged in parallel columns, one in German and the other in English. An added convenience is the placing of English titles on the margins of the text. The literature was carefully covered to the close of 1949, and used to give thorough documentation to the material. Some sections were supported by references as late as 1959. The tables of information far outnumber the 133 figures. The organization, scope and character of this book make it an invaluable addition to this most important reference work, particularly as a quick source of information and as a lead to the important primary sources.

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Wooster, Ohio

Gmelins Handbuch der Anorganischen Chemie, 8. Auflage, System-Nummer 52, Chromium. Part A, Section 1

Edited by the Gmelin Institute under the direction of *E. H. E. Pietsch*. Verlag Chemie, GMBH, Weinheim, Bergstrasse, 1962. xx + 418 pp. Figs. and tables. 18 × 25.5 cm. Cloth bound, $79.

Most of this book (284 pages) deals with the history, occurrence and technology of chromium. After a short (5 pages) section on the history, the part on occurrence is given under the following heads: extraterrestrial occurrence, geochemistry, economic deposits, and minerals. The technology part deals with ore dressing, treatment of chromite, production of chromium, manufacture of inorganic chromium compounds, manufacture of inorganic chromium dyes, and industrial hazards. This is followed by a ten-page section on toxicity.

Only the beginning of the discussion of the element, chromium, itself is included in this current volume. This includes nine pages on the formation and preparation of the element, and 125 pages on its physical properties. The latter include, among others, the crystallographic, mechanical, thermal, optical, spectral and magnetic properties.

As with other recent volumes of this work, the Contents are given in parallel German and English columns, and English titles are used in the margins of the text. Likewise, the literature search has been thorough only to the end of 1949, but the reviewer noticed that special portions were supported by references as late as 1959.

John W. Chittum
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Wooster, Ohio

Bernice T. Eiduson, University of Southern California, Los Angeles. Basic Books, Inc., New York, 1962. 266 pp. Tables. 15.5 × 21 cm. $6.50.

Dr. Eiduson presents an extensive and intensive study of forty distinguished research scientists (including two Nobel Prize winners) who have positions at far west academic institutions and whose fields of study include physics, earth sciences, chemistry, and biological sciences. The scientists are diverse with respect to age, socio-economic background, and parental occupation.

The methods employed by the author primarily involved interview and projective tests. The results and interpretations are organized into five main sections, and within each section, Dr. Eiduson attempted to determine what findings, if any, were common to the members of the group and what interesting finding may be unique to a particular scientist.

The personal history. Four characteristics are especially emphasized. First, as children, the scientists somewhat lacked close relationships, especially with respect to their fathers. Second, at some period in the child's life, he experienced isolation. This yielded, according to Dr. Eiduson, a looking inward for resources and amusement. Third, the superior intellectual ability of the scientist was observed at an early age. Fourth, the scientists did not indicate that one factor, such as a stimulating teacher or a chemistry set, was influential in developing their scientific interest.

Adult personality structure. The emotional life of the scientists is heavily invested in intellectual pursuits. In conjunction with this tendency, the men have developed habits of adjustment which do not permit extreme emotional involvement outside of their work. Anxieties that do exist are not general, but related to specific areas of interest. In addition, the scientists are highly sensitive, especially to fine sensory discriminations and to their own motivations.

Styles of thinking. Dr. Eiduson's group is most homogeneous in this area. The men tend to recombine concepts and obtain what is important from their environment in a highly selective manner. The theoreticians, referred to as the aristocrats of science by the scientists, are not different from the experimentalists in terms of perceptual-cognitive processes.

The self-image as members of the scientific community. The scientists identify with great discoverers. One reason for the persistence of this view is that each discovery, no matter how small, contributes to scientific development. A second reason is that great discoveries, in retrospect, appear simple and each scientist feels the great discovery is within his grasp.

Dr. Eiduson indicates that the men of her study find "happiness in pursuit." Their strong drive toward their work, suggestive of compulsiveness, is exhibited by their ability to find research time despite the demands of teaching and/or administrative duties. Similarly, the scientists of Dr. Eiduson's study expressed

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reservation with respect to a new "gentleman scientist" who works from 9 to 5 and pursues other activities.

Scientific life style. With respect to home life, the men lead middle-class lives and their work is virtually unknown to their family. They report the role which is most difficult is that of a parent. With respect to community life, the men generally abstain from intellectualism in the lay community. With respect to recreation, leisure activity is a means the scientists use to rest and rebuild their mental strength. The scientists, Dr. Eiduson concludes, do not show their best part when they are away from the academic community.

The general impression of the reviewer is that the book has the virtue of a simple style which weaves the individual case with the scientists as a group into a nonsystematic, but meaningful pattern. In addition, the book has, with a few exceptions, a minimal amount of depth interpretation, i.e., the author has not attempted to find "dynamic factors" that are the "real causes" of the scientists' behavior.

On the negative side, the major problems involve the method of study rather than the presentation. There is occasional difficulty in knowing where data stop and opinions begin. Also, the scientists likely knew they were being studied because of their scientific interests and the question of what influence this knowledge may have had upon their responses may be raised.

The lack of a control professional group with similar intellect and background makes it extremely difficult to identify characteristics uniquely related to scientists.

In summary, the book provides an opportunity for scientists to use their narcissistic tendencies and partake in reflective reading.

James Voss
College of Wooster
Wooster, Ohio

Chem Sources

4th ed. Directories Publishing Co., New York, 1962. 476 pp. 23 × 29 cm. $22.50.

There are 24,000 listings of chemicals, abietic acid to zymosan, with at least one supplier identified. No further information (such as price or quality) is given, but the producer is identified in case of the rarer items.

The listing is alphabetical: dichloropropane is in the D's; *p*-tert Butyltoluene is in the B's. Many radioisotope-labeled compounds are included. Very probably the book will be useful to those who, in the words of the preface, want to "reduce costs associated with the procurement function." College professors who *buy* things probably will not want to spend $22.50 for this book.

W. F. K.

Harold A. Scheraga, Cornell University, Ithaca, New York. Academic Press, Inc., New York, 1961. xiv + 305 pp. Figs. and tables. 15.5 × 23.5 cm. $8.

This book, the first volume in a new monograph series on Molecular Biology, is based on lectures delivered at the Wool Research Laboratories, Melbourne, Australia in 1959. The author, Harold Scheraga, has contributed extensively to protein chemistry. He has written an interesting book emphasizing areas where he is an authority. Over 50 references describe his own work. The book is not an exhaustive discussion of protein chemistry however; it is a coherent development of several major aspects of this field.

There are seven chapters. The first chapter, Hydrodynamic Properties of Protein Solutions, is an excellent introduction in which a number of references to more rigorous discussions are included. This chapter would be valuable as a supplement to the usual graduate lectures.

The next three chapters include: Internal Structure; Effect of Hydrogen Bonding on Side-Chain Reactivity, Limited Proteolysis, and Denaturation. Denaturation is defined and then discussed in relation to the elastic properties of protein fibers, equilibrium in solution, and kinetics in solution. These chapters are then illustrated through a discussion of the fibrinogen-fibrin conversion in Chapter V.

Experimental methods in Chapter VI are limited to optical rotation, deuterium-hydrogen exchange, infrared absorption spectra, and ultraviolet absorption spectra. Experimental methods are then applied to the determination of protein structure. Insulin, lysozyme, and ribonuclease are chosen as examples in Chapter VII. The publication of new data on protein structure is so rapid that information discussed here will have less value than the more general discussion of concepts and methods.

This book is not a substitute for the many extensive monographs on protein chemistry which are available. For example, the section on optical rotation is much less inclusive than a recent review by Urnes and Doty. Scheraga discusses protein structure from a broad perspective. His monograph has much of the clarity and interest of a good lecture course. The book is valuable for teachers and should be available both in their personal libraries and the university library.

David G. Cornwell
Ohio State University
Columbus

Molecular Biochemistry

Edward M. Kosower, State University of New York, Long Island Center, Stony Brook. McGraw-Hill Book Co., Inc., 1962. xii + 304 pp. Figs. and tables. 16 × 24 cm. $12.50.

Despite the large number of scientific books currently available, outstanding ones, those that combine critical review, significant correlations and new interpretations, are still rare. "Molecular Biochemistry" falls squarely into this select category.

Professor Kosower defines Molecular Biochemistry as "a new research area which has emerged from the application of the physical-organic approach to the problems in chemical transformation found in biochemistry." He skims the field of biologically important topics to cover only those that are related to extensively studied chemical processes or those that have recently received attention from chemically oriented investigators. The metabolism of sulfate compounds or the chemistry and stereochemistry of glycolipid reactions are not mentioned, for example, presumably because physical-organic techniques have not been applied sufficiently in these areas. On the other hand, Taft's work on acid catalyzed hydrations and the Hammett-Deyrup acidity function are introduced, although it is unlikely that any biological analogy can ever be found for hydration in strong acid solutions. As in a lecture series, we are presented with selected topics, grouped in three main sections.

The first section, Biochemical Patterns, devotes sixty pages to the stoichiometry of some significant reactions of intermediary metabolism and includes a discussion of biosynthesis. Transformations and cycles are summarized and different reaction "types" tabulated. Kosower's comments on the relative frequency of "types" have little significance, however, because of the limited choice of topics.

The main part of the book, Chemical Patterns, consists of a careful discussion of fourteen reaction types, based partly on those encountered in the initial review. Typical headings include decarboxylation, hydrolysis: esters and oxidation-reduction: one electron transfer. The biological reactions are thoroughly correlated with similar chemical reactions, and many glib claims made by optimistic chemists and biologists are shown to be inadequate. The discussion is strictly in terms of reaction mechanisms. Unfortunately, this implies that biological reactions can be understood in terms of model systems. Although the book deals exclusively with enzyme catalyzed reactions, nowhere is the problem of enzyme specificity extensively discussed.

The last twenty pages, Physical Patterns, mention many perplexing problems which stem from the fact that "the most important materials present in biological systems act primarily by virtue of their physical properties rather than by taking part in chemical transformations." A discussion of the "active site" problem fills most of this section, concluding with Kosower's own solution for "mapping" the active site of an enzyme. The experiment suggested is ingenious but not as conclusive as he would like. Since it requires isolation, or at least slow formation, of a stabilized acyl-enzyme intermediate, it is subject to ambiguous interpretation. Only those experiments which could examine the enzyme-substrate complex without disturbing the normal reaction sequence would truly deserve to be called "direct."

It is possible to question Kosower's

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OUTLINES OF BIOCHEMISTRY

By ERIC E. CONN *and* P. K. STUMPF, *both of the University of California at Davis.* Here is a modern, over-all picture of the rapidly expanding science of biochemistry, written for those who have had an introductory course in organic chemistry. The authors deal with the fundamental aspects of intermediary metabolism of the primary cell constituents—carbohydrates, amino acids and proteins, lipids and nucleic acids; and they discuss in some detail modern aspects of biochemical genetics. They include a review of the necessary chemistry and introduce the subject of coenzymes and enzymes. The student is also provided with an excellent opening chapter covering the often misunderstood subjects of *p*H and buffers, with numerous examples and problems in the appendix.

Important features are: emphasis on the electronic aspects of biochemical reactions; reviews of concepts of modern biochemistry throughout the book; a list of modern biochemical methods permitting the student to acquaint himself with each method as it is mentioned in the book; treatment of vitamins from the point of view of coenzymes, stressing their mechanism of action; use of illustrations to point out the active site of the biochemical reaction; and an easy-to-follow presentation of important metabolic schemes. *1963. Approx. 416 pages. $8.75.*

METHODS OF BIOCHEMICAL ANALYSIS
Volume XI

By DAVID GLICK, *Stanford University Medical School.* This volume is the eleventh of a well-known series that reviews the methods and techniques in the field of biochemical analysis. Both well-established methods or techniques that have undergone sufficient improvement to merit reappraisal, and new approaches which bear promise of great usefulness are included. Each chapter offers a background discussion of previous work, a critical evaluation of various approaches, and a presentation of the procedural details of the method or methods recommended by the author. *1963. 442 pages. $14.50.*

TREATISE ON ANALYTICAL CHEMISTRY
PART II: ANALYTICAL CHEMISTRY OF THE ELEMENTS
Volume 8

Edited by I. M. KOLTHOFF, *University of Minnesota; and* PHILIP J. ELVING, *University of Michigan; with the assistance of* ERNEST B. SANDELL, *University of Minnesota.* The latest volume in a systematic and comprehensive treatment of all aspects of modern analytical chemistry, this book contains authoritative material on the analytical chemistry of the rare earths and of the platinum metals. An Interscience Book. *1963. Approx. 562 pages. $20.00.*

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Edited by CALVIN W. TAYLOR, *The University of Utah; and* FRANK BARRON, *The University of California, Berkeley.* This book gives selected papers from the Proceedings of the First, Second, and Third University of Utah Conferences: "The Identification of Creative Scientific Talent," supported by the National Science Foundation. Leading figures in the psychology of creativity present theoretical as well as empirical findings as an impetus to further study and research. *1963. 419 pages. $8.75.*

MOLECULAR VIB-ROTORS
The Theory and Interpretation of High Resolution Infrared Spectra

By HARRY C. ALLEN, Jr., *National Bureau of Standards; and* PAUL C. CROSS, *Mellon Institute.* This book covers the theory of the vibrating-rotating molecules, energies, selection rules, and line strengths. Theory is developed starting with the derivation of the general Hamiltonian. The Hamiltonian is solved in the rigid rotor approximation, and the solutions discussed in detail. *1963. Approx. 384 pages. Prob. $15.00.*

LATEX FOAM RUBBER

By E. W. MADGE, *Dunlop Rubber Co. Ltd.* This book is concerned with an exposition of the fundamental technical 'know-how' on which the latex foam rubber industry is based. Technical factors affecting both production and marketing are considered. An Interscience Book. *1963. 270 pages. $9.00.*

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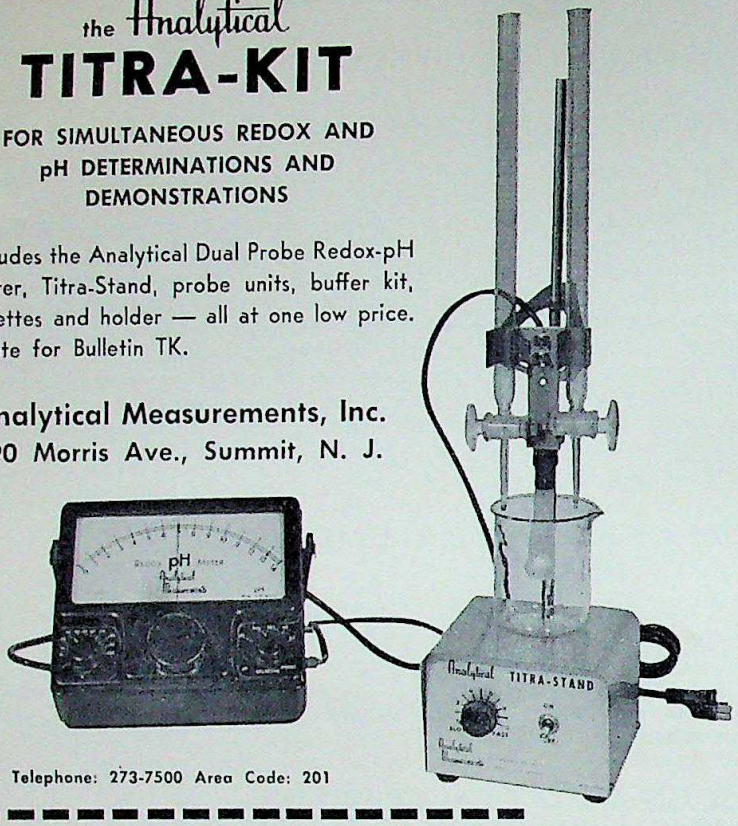
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choice of topics, his emphasis and his conclusions. But this only indicates that he has selected, judged and proposed. The omission of some areas which have received little attention from physical-organic chemists is unfortunate precisely because these could benefit greatly from his critical attention. Finally, one cannot discuss "Molecular Biochemistry" without reference to the multi-lingual quotes used as section headings. These little phrases are seldom charitable but always diverting.

GEORGE E. HEIN
Boston University
Boston, Massachusetts

Horizons in Biochemistry: Albert Szent-Györgyi Dedicatory Volume

Edited by *Michael Kasha*, Florida State University, Tallahassee, and *Bernard Pullman*, Université de Paris, France. Academic Press, Inc., New York, 1962. xiv + 604 pp. Figs. and tables. 16.5 × 23.5 cm. $16.

This fine book dedicated to Albert Szent-Györgi is an interesting and stimulating collection of essays by an international group of 28 leading scientists. Their writings cover new concepts, new analyses, and physiological viewpoints concerning modern biochemistry and molecular biology. Each contributor was especially asked to express new views directed toward modern biochemistry and toward its future. In this, the Editors were fully rewarded.

Chapters are as follows: Albert Szent-Györgi and Modern Biochemistry by René Wurmser, Biochemical Evolution by J. D. Bernal, Evolutionary Possibilities for Photosynthesis and Quantum Conversion by Melvin Calvin, On Dating Stages in Photochemical Evolution by Hans Gaffron, Origin and Evalution of Bioluminescence by W. D. McElroy and H. H. Seliger, On the Problems of Evolution and Biochemical Information Transfer by Alexander Rich, Life in the Second and Third Periods; or Why Phosphorus and Sulfur for High-Energy Bonds by George Wald, A Biochemical Approach to Genetics by Lernom M. Ingram, Enzymatic Mechanisms in the Transmission of Genetic Information by Severo Ochoa, A "Book Model" of Genetic Information-Transfer in Cells and Tissues by John R. Platt, Molecular Disease Evolution and Genetic Heterogeneity by Emile Zuckerkandl and Linus Pauling, The Significance of Absolute Configuration and Optical Rotation in Catalysis by Henry Eyring, Leon L. Jones, and John E. Spikes, On the Metabolic Significance of Phosphorolytic and Pyrophosphorolytic Reactions by Arthur Kornberg, Catalysis in Life and in the Test Tube by D. E. Koshland, Jr., Enzyme Activity and Cellular Structure by H. A. Krebs, Giant Molecules and Semiconductors by L. Brillouin, Is DNA a Self-Duplicating Molecule? By Barry

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By ROBERT M. SILVERSTEIN *and* G. CLAYTON BASSLER, *both of the Stanford Research Institute.* Written for students of organic chemistry, this book shows how to identify organic molecules by recording their responses to four energy probes as mass, infrared, nuclear magnetic resonance, and ultraviolet spectra. It is oriented toward the rationalizations involved in translating spectra in chemical structures. The authors achieve a level of sophistication that permits solution of problems ranging from the identification of rather simple compounds, about which little or no information is available, to elucidation of structural details of complex molecules, about which quite a bit is known. *1963. 177 pages. $8.50.*

CHEMICAL CALCULATIONS
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THE CHEMISTRY OF WOOD

Edited by B. L. BROWNING, *The Institute of Paper Chemistry.* A fresh look at concepts and the state of knowledge in the important area of wood chemistry, giving recent developments in the field. The book presents the outstanding features of the chemistry of wood and its components. Although it is sufficiently detailed to serve as a reference, the book is primarily aimed at the student, the young scientist in wood-using industries, and the scientist and technologist wishing critical surveys of the topics in the field. An Interscience Book. *1963. Approx. 736 pages. Prob. $24.50.*

MAGNETISM AND THE CHEMICAL BOND

By JOHN B. GOODENOUGH, *Massachusetts Institute of Technology.* A comprehensive survey of the current position of research into the magnetic interactions of transition metal ions in their solid compounds. Emphasis is on a physical description of concepts that appear to operate in a similar manner over the whole range of crystalline materials, from ionic insulators to metals. These interpretations not only support some of the extrapolations that are asserted, but also provide the chemist with a physical intuition that can be fruitful for the design of materials with specified characteristics. This volume initiates a series of monographs on Inorganic Chemistry. Volume 1 in the Interscience Monographs on Chemistry—Inorganic Chemistry Section. *1963. Approx. 398 pages. $12.50.*

THE CYANINE DYES AND RELATED COMPOUNDS
THE CHEMISTRY OF HETEROCYCLIC COMPOUNDS—Volume 18

By F. M. HAMER. A complete and systematic treatment of the chemistry of the cyanine dyes, this volume continues a series of monographs that gives up-to-date, detailed, and comprehensive presentations of the various branches of heterocyclic chemistry. An Interscience Book. *1963. Approx. 808 pages. Prob. $25.00.*

CHEMICAL ANALYSIS BY FLAME PHOTOMETRY

By ROLAND HERRMANN, *University of Giessen, Germany; and* C.T.J. ALKEMADE, *The University of Utrecht. Translated by* PAUL T. GILBERT, Jr., *Beckman Instrument Inc.* A comprehensive introduction to the technique and results obtained by flame photometry. Volume XIV in the Interscience Chemical Analysis Series. *1963. Approx. 432 pages. Prob. $13.50.*

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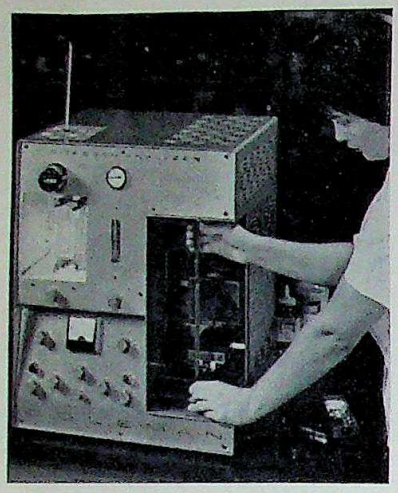
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Each subject is treated in a factual and exciting manner. The book can be enjoyed by the general reader of science and will reward him by the easy style, the up-to-date views, and stimulating insight into the future of biochemistry. This book is highly recommended to biochemists and general readers in science.

Roy L. Whistler
Purdue University
Lafayette, Indiana

Hydrogen Compounds of the Group IV Elements

F. G. A. Stone, Harvard University. Prentice-Hall, Inc., Englewood Cliffs, New Jersey, 1962. 112 pp. Tables. 15.5 × 23.5 cm. $5.25

The purpose of this short volume is to remedy the lack of attention by reviewers to the advances in the chemistry of hydrogen compounds of silicon, germanium, tin and lead. The volume is not designed to be comprehensive, but is to provide the reader with a survey of the work.

There are 112 numbered pages, of which seventeen are consumed by the references. The remaining pages are distributed as follows: Eight pages are given to "general considerations" in which the four elements are contrasted to carbon in terms of the modes of chemical bonding, relative electronegativities, bond strengths of M-H and M-M linkages, and the relative reactivities of these bonds. Twenty-five pages are devoted to the silicon hydrides and related compounds. The organization of this chapter is the model for the remaining chapters. The preparative methods are followed by a section on the chemical and physical properties. Here, occasional reference is made to the mechanism of a reaction. The third section is devoted to derivatives of silane, such as halosilanes, compounds with elements of the V and VI th groups, and organosilicon hydrides. Discussions on mechanisms of reaction and bonding are included in this section. The last section is devoted to the thermochemical, electron diffraction, and spectroscopic studies on these compounds. The germanium hydrides and related compounds are discussed in fourteen pages, stannum hydrides in ten, and plumbum hydrides in a little more than two pages. Within these pages eight tables of data are included. Many complete equations are presented, although by some oversight about a dozen equations lack all the products.

The book is attractively made up, with each chapter introduced with a page (numbered) solely devoted to a large white H on a gray background overprinted with the name of the element.

Edwin Larsen
University of Wisconsin
Madison

Clathrate Inclusion Compounds

Sister Martinette Hagan, Mundelein College, Chicago. Reinhold Publishing Corp., New York, 1962. xiii + 189 pp. Figs. and tables. 13.5 × 19.5 cm. $6.50.

This is a little book: only 19.5 × 13.5 × 1.7 centimeters outside, and only 6 chapters in the middle of barely 200 pages inside. But it covers the subject matter of 319 references well. The first chapter logically defines the area of inclusion compounds to be dealt with, and the other five successively discuss the structure, properties, preparation, use, and future of clathrates. Logic would have put preparation before structure and properties, but the reverse works out satisfactorily.

The inclusion compounds were really a discovery of the 1940's, although examples were known earlier. From Bengen's urea adducts of *n*-alkyls, and Powell's quinol complex of argon, evolved the exciting revelation of a whole new set of solid substances, in which flat, long, or small molecules are trapped in one, two, or three dimensions within the crystals of another. Researchers, teachers, and students alike recognized that here was confirmation of the entire imaginary world of molecules. By largely restricting her book to those substances formed by entrapment in three dimensions, or clathrates, the author misses a little of both the excitement and the beauty of the field.

Chapter 2 presents the structure revealed by examining with X-rays the clathrates of quinol, tri-ortho-thymotide, cycloveratril, water, phenol, amine complexes of metal cyanides, Dianin's compound, and others. Diagrams taken from the original papers illustrate each structure.

Chapter 3 discusses various properties of clathrates derived from inert gases, methyl compounds, *n*-alkyls, arenes, simple inorganic compounds, and so on. Tables taken from the original papers list some of them.

Chapter 4 describes the methods used to form clathrates from the hosts of Chapter 2 and the guests of Chapter 3. Solvents to dissolve the hosts and modest pressures to increase the concentration of the guests are helpful. Astonishingly little work seems to have been done upon the rate and kinetics of clathration.

(*Continued on page A224*)

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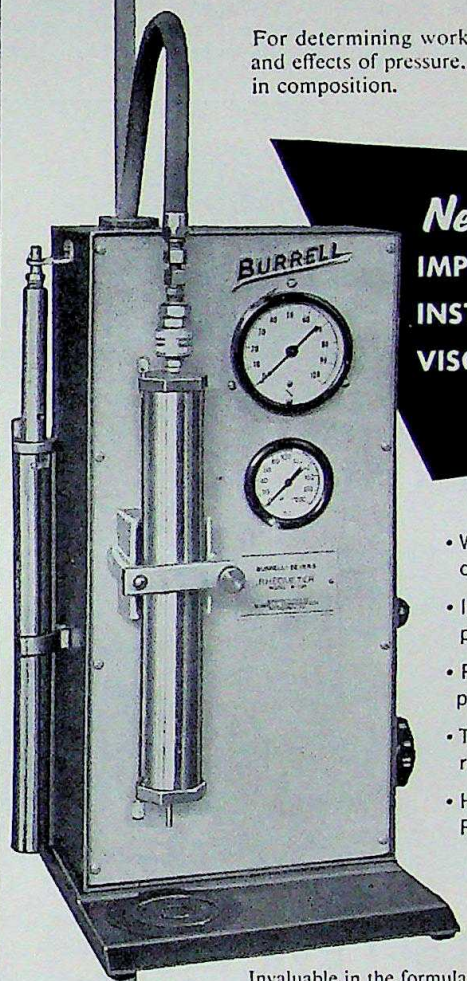
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Chapter 5 runs into a problem: clathrates have as yet had little use: separation of rare gases, purification of benzene, concentration of arene isomers, freshening of water. In order to say more, the author has had to include some work on inclusion compounds entrapped in only two dimensions, rather than all three.

Not until almost the final chapter does a little of the feeling of the author show through. The reader has to be content with: ". . . evidently clathrate compounds have often been prepared by many an unsuspecting chemist," ". . . compounds that have been with us a long time, but whose existence and potential we have been slow to recognize," and " . . . a whole new field of investigation which does not lack direction though, at present, it lacks order." She could have improved the original diagrams, shown anomalies in original data, and criticized conflicting views, instead of just presenting things as they are.

But presenting clathrates as they are has advantages. Every chemist in training ought to be aware that they have always existed, that chemists missed them and still have only scratched the surface, and that anyone can learn more about them. There is no better field for a first research project than inclusion compounds. That is probably why this little book was written the way it was and why it should certainly be read by every teacher and student of chemical research.

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A Guidebook to Mechanism in Organic Chemistry

Peter Sykes, Cambridge University, England. John Wiley and Sons, Inc., New York, 1961. xiii + 247 pp. Figs. and tables. 14 × 21.5 cm. $3.95.

This book can serve as an introduction to modern concepts of organic chemistry for those who have learned from most of the elementary texts. The topics covered include structure, acids and bases, substitution reactions, addition reactions, carbonium ions, carbanions, and radicals. A general knowledge of organic chemistry is presumed.

The presentation is rather wide ranging: individual items are treated quite briefly as befits the title. This is clearly a guidebook. In general the concepts are presented with reasonable accuracy, though often in a somewhat outdated or oversimplified form. The outlook of the book is comparable to that of Ingold's "Structure and Mechanism in Organic Chemistry," though the coverage is considerably broader.

Sykes should be compared with Hines' "Physical Organic Chemistry" or with Gould's "Mechanism and Structure in Organic Chemistry." These two are much longer, and more expensive, but they also provide better balance and accuracy as well as being more comprehensive.

Sykes' book might be suitable for a senior seminar or for independent study by an advanced undergraduate student. It would not be suitable for use by graduate students. Nor would it be particularly useful to a student who had studied from a text such as Morrison and Boyd or Cram and Hammond.

D. F. DETAR
Florida State University
Tallahassee

Mechanism of Sulfur Reactions

William A. Pryor, Purdue University, Lafayette, Indiana. McGraw-Hill Book Co., Inc., New York 1962. xiv + 241 pp. Figs. and tables. 16 × 23.5 cm. $9.75.

This little monograph is a welcome addition to the growing list of books on organic sulfur chemistry. As recently as 1958, there had been only one attempt to summarize the enormous volume of literature in this fascinating but complicated field. Since then, several volumes have been published, and two series of monographs initiated. The book by Pryor

(*Continued on page A226*)

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does not duplicate other efforts, but supplements them. He has summarized many studies on mechanisms of sulfur reactions, and offered selected examples which supply evidence for these mechanisms.

After an introduction which includes nomenclature, the reactions and properties of elemental sulfur are considered. Then the whole group of thiols, disulfides and polysulfides is discussed. First the physical characteristics, such as bond lengths, energies and angles, are reviewed, including a good summary of the evidence for d-orbital overlap in organic sulfur compounds. Then follows an excellent review of the evidence for homolytic cleavage of the disulfide bond. The discussion of heterolytic cleavage is less satisfactory. The author has relied heavily on recent articles in *Chemical Reviews* for this section. The discussion of nucleophilic attack on the disulfide bond, which has been reviewed by Parker and Kharasch, is well annotated, but the subject of electrophilic attack is summarized in slightly more than two pages, and the whole system of acid catalyzed cleavage reactions is limited to a reference to chlorination of disulfide, which may or may not proceed *via* a sulfenium ion, as suggested on page 59.

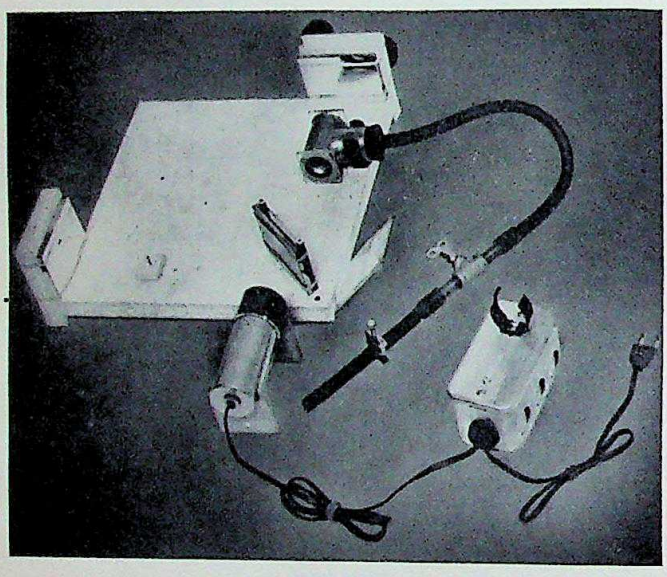
The following five chapters deal with the authors special field of interest, the oxidation, dehydrogenation, and sulfurization of hydrocarbons and other organic compounds. Many industrially important reactions, such as vulcanization, are included. In this area Dr. Pryor is an obvious authority, and these chapters give the book its greatest value. Chapters 10 and 11 provide a useful supplement of examples of experimental procedures, and a table of several hundred compounds which have been oxidized by sulfur. Some of the products shown are remarkable, and will offer the arm-chair mechanist some real food for thought.

The text is clear and readable, and remarkably free from error for a book which contains so many structural formulas. This book will be a useful source volume for advanced courses in mechanisms of reactions, and as a library reference.

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Comprehensive Biochemistry. Volume 2, Organic and Physical Chemistry

Edited by *Marcel Florkin*, University of Liège, Belgium and *Elmer H. Stotz*, University of Rochester School of Medicine and Dentistry, Rochester, New York. American Elsevier Publishing Co., Inc., New York, 1962. xii + 328 pp. Figs. and tables. 15.5 × 23 cm. $14.50.

This volume is the second in the section of "Comprehensive Biochemistry" devoted to physico-chemical and organic aspects of biochemistry. The book contains three chapters: Mechanisms of Organic Reactions by M. L. Bender and R. Breslow; and Behaviour of Molecules in Solution; and Diffusion and Osmosis, by W. D. Stein.

In the reviewer's opinion, Bender's treatment of mechanism of organic reactions will prove invaluable to any biochemist who is concerned with the mechanism of an enzymatic process. This chapter represents one of the most complete reviews of analogies between organic and enzymatic systems to be found in the current literature. It is understandable that most attention has been paid to non-oxidative reactions since the best enzyme models are to be found in this area. In the relatively brief section on oxidation-reduction systems no discussion is made of flavoenzyme catalysis. Albeit, the authors are to be commended for an excellent review. The text is well complemented by clearly drawn formulas.

The last two chapters in this volume, by Stein, are beautifully written. The discussion of solutions proceeds logically through four sections: small nonelectrolytes, small electrolytes, polymers, and finally, polyelectrolytes and proteins. The last chapter is concerned with the molecular-kinetic basis of diffusion, osmosis, and viscosity. Although the various equations pertinent to these phenomena are not derived, adequate references are presented for this purpose.

It cannot be denied that "Comprehensive Biochemistry," when completed, will be an often consulted reference series for all biochemists "at the bench." It will also be a welcome reference for the instructor and the more advanced student

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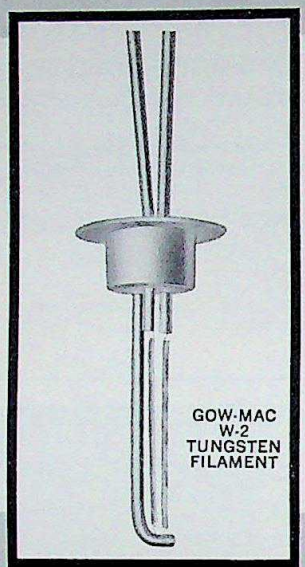
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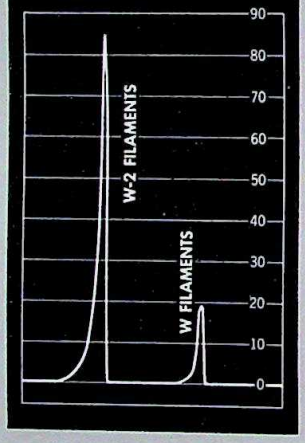
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E. L. Gefter, Academy of Sciences, U.S.S.R. Translated by *G. M. Kosolapoff*, Auburn University, Alabama. Trans. ed. by *Leon Jacolev*, Associated Technical Services, Inc., Glen Ridge, New Jersey. Associated Technical Services, Inc., 1962. xix + 288 pp. Figs. and tables. 17.5 × 26 cm. $14.75.

The present monograph is the first to appear which deals with heteroorganic polymers other than those containing nitrogen and silicon. The author has attempted to generalize and systematize the existing information concerning the synthesis and physical properties of polymers containing phosphorus as a constituent in the main skeleton or in side chains. In addition, considerable attention has been paid to synthetic methods leading to monomers of use in polymerization reactions. Much of the information concerning both monomers and polymers is presented in easily accessible tabular form; included here are such items as reaction conditions, nature of the reaction product, yields, analyses, and certain physical data.

One very helpful feature is the inclusion of a section on nomenclature. The United Kingdom and United States of America journals use the system proposed by joint agreement in 1952 and which has been recognized by the International Union of Pure and Applied Chemistry (1960). Although agreement on this score is far from unanimous and is not practiced in non-English-speaking countries, the translator has used the "new" system and included parenthetically some of the more familiar "old" names in preparing illustrations of name types.

Part I of the monograph (136 pages) describes the chemistry and properties of starting materials used for the preparation of organophosphorus high polymers. Chapter I deals with unsaturated organophosphorus compounds. Included in the discussion are certain unsaturated acids and their derivatives such as esters formed from acids and unsaturated alcohols, vinyl compounds, and unsaturated phosphines, their oxides and related compounds. Chapter II concerns the preparation and properties of saturated organophosphorus compounds having reactive functional groups as, for example, the dichlorides of some saturated acids of phosphorus, polyhydroxyl compounds, polycarboxylic acids and their esters, amides, etc. Chapter III provides tables of the refraction of some

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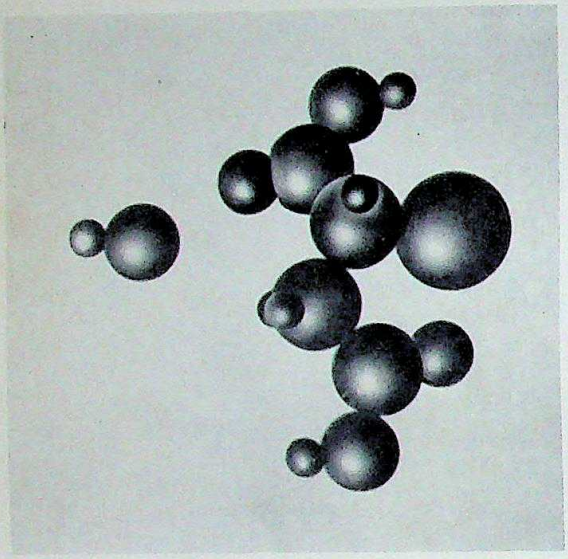
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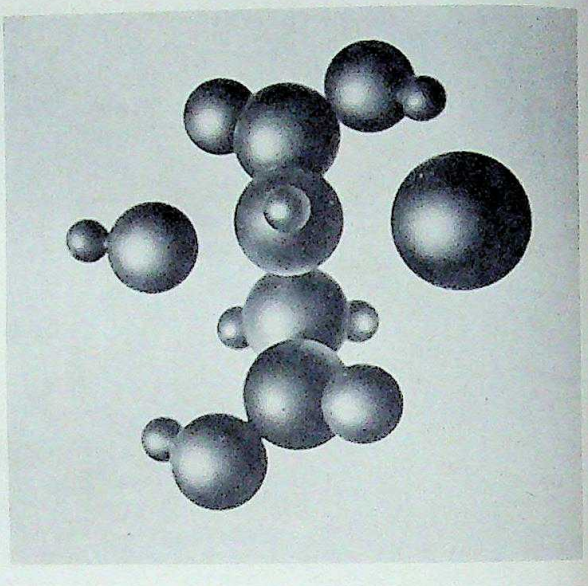
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The Preface of this book begins by saying, "Teaching—and learning—organic chemistry can be a highly satisfying experience because of the logic and consistency inherent in this science." In keeping with this spirit Dr. Gero's presentation is highly lucid and well-organized, and will be greatly appreciated by students.

It is a **teaching** text for the average student—one that presents organic chemistry as an exercise in reasoning and understanding rather than memorization. Although it covers a great deal of material, it offers penetrating explanations of subtle and difficult points.

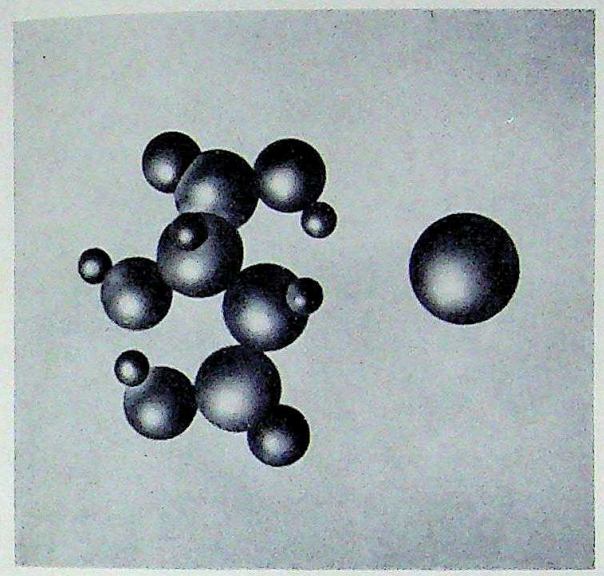
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By Alexander Gero, Associate Professor and Director of the Laboratory of Organic Chemistry, Department of Pharmacology, Hahnemann Medical College, Philadelphia.





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1963. 679 pages. 6¾ by 9⅝. Illus. $9.50.

ABOUT THE AUTHOR . . .

Alexander Gero is unusually well qualified to write this text: In addition to being engaged for 17 years in industrial research, he has had extensive experience in teaching chemistry to undergraduate, graduate, and medical students. After receiving his Ph.D. in Chemistry in 1930 from the University of Vienna, he served as a research chemist and executive in the chemical and drug industry in Europe, South America, and the United States until 1947.

He was affiliated with Villanova University as an Assistant Professor, and later as an Associate Professor of Chemistry from 1947 to 1952. From 1952 to the present he has been associated with Hahnemann Medical College, Philadelphia, where he is Associate Professor and Director of the Laboratory of Organic Chemistry in the Department of Pharmacology. He is a Fulbright lecturer in Spain for the academic year 1962-63.

Dr. Gero holds several American and foreign patents from his past industrial experience, and he has written a textbook (on Biological Chemistry) and 27 papers in the field.

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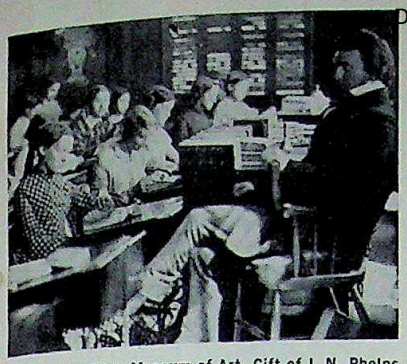
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BOOK REVIEWS

atomic groups of organophosphorus compounds.

Part II of the monograph (114 pages) deals with the chemistry of high polymers. Chapter IV describes carbon-chain and hetero-chain polymers containing phosphorus in the side chains. Examples of subjects dealt with in this chapter are polymers and copolymers of amides, amide esters and ethylenamides of phosphorus acids, and carbon-chain products of polycondensations of organophosphorus compounds. Chapter V is concerned with heterochain high polymers containing phosphorus in the main chain. Examples here include polymers having phosphorus and carbon in the main chain or those containing phosphorus, oxygen and carbon or phosphorus, nitrogen and some other element in the main chain. Polymers with a purely inorganic skeleton are also considered as, for example, those having phosphorus, oxygen, and boron in the main chain. Chapter VI deals with miscellaneous products of undetermined structure and considers products of telomerization with participation of organophosphorus compounds. Chapter VII considers applications of organophosphorus polymers. Topics discussed include uses in plastics and as flame-resistant coatings, adhesives, oil additives, and catalysts.

The bibliography contains 834 references, some of which are multiple listings. All have been carefully checked and verified with the exception of 22 references which could not be checked because journals or patents were not available. Very adequate indices of tables and subjects are given.

This reviewer feels that the monograph is excellently done and represents a valuable addition to the chemical literature. It should be welcomed particularly by those involved in specific problems relating to the practical uses of polymer systems. It is, however, a valuable source of collected information in the field of organophosphorus compounds for those generally concerned with the theory and practice of polymer chemistry.

E. Charles Evers
University of Pennsylvania
Philadelphia

Scientific Method: Optimizing Applied Research Decisions

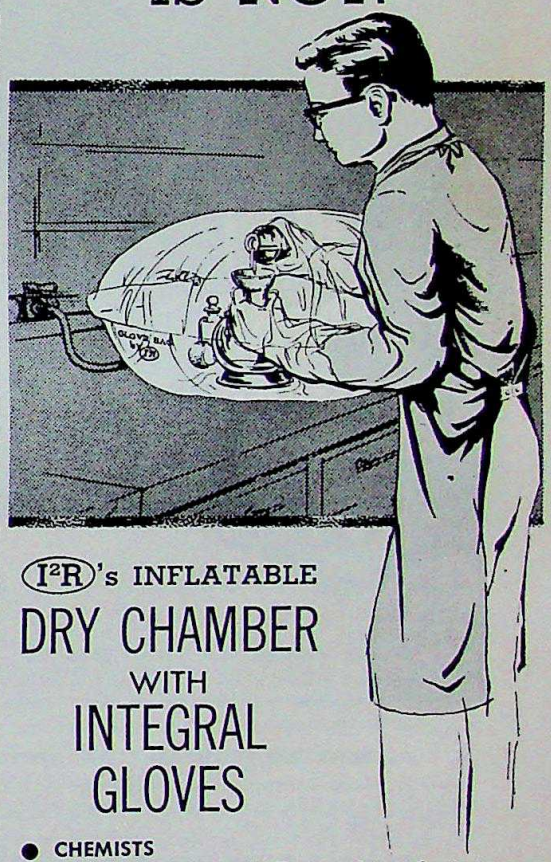
Russell L. Ackoff, with the collaboration of *Shiv K. Gupta* and *J. Sayer Minas*, Case Institute of Technology, Cleveland, Ohio. xii + 464 pp. Figs. and tables. John Wiley and Sons, Inc., New York, 1962. 15.5 × 23.5 cm. $10.25.

As the author states in his preface, this is a "book on planning or designing the use of science in the pursuit of objectives.... It is essentially a 'how to do it' book rather than a 'what to do it for' book.... This book is intended to improve the

(Continued on page 1234)

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skill of the scientist in the conduct of inquiry . . . and my objective will have been accomplished if I succeed in attracting a few scientists to the study of scientific inquiry in its own right and if a few more find ways of improving their research procedures."

Because this review will appear in a journal quite far removed from the immediate interest of the book's author, it seems appropriate to consider the benefits it might afford a more casual reader, other than the student enrolled in a course in Operations Research for whom it obviously is intended. The key to the book is contained in the first sentence in Chapter 3: "In applied research, it is necessary to [illegible] decision maker's problem into a research problem." Chapter 13 reviews the techniques of testing and controlling the model and the solution to the problem, resulting from the research. In between these chapters, the bulk of the book is concerned with the techniques of this kind of research: formulating the problem, models, defining, measurement, sampling, estimating, testing hypotheses, experimentation and correlation, deriving solutions from models, and experimental optimization. Each chapter has an extensive bibliography.

The last two chapters (14 and 15) are particularly provocative: Implementation and Organization of Research, and The Ideals of Science and Society. Even the non-specialist will derive benefit from reading these, as they relate to so many pressing current problems like "conflict between science and other social institutions," "dissemination of research findings," "the research team," and "the ideals of man," to cite a few section headings. The concluding sentence to Chapter 15 "is: To be sure, responsibility for future morality is not the scientist's alone, but perhaps from him can come leadership in the substitution of brain for brawn in settling conflicts between men and between their societies."

LAURENCE S. FOSTER
Army Materials Research Agency
Watertown Arsenal
Watertown, Massachusetts



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Lehrbuch der Organischen Chemie. Band 2

Friedrich Klages, University of Munich, Germany. 3rd ed. Walter de Gruyter and Co., Berlin, 1962. xiv + 639 pp. Figs. and tables. 18 × 24.5 cm. 56 DM

Klages' "Organic Chemistry" is a remarkable textbook. The entire set consists of three volumes arranged in four books containing more than 2500 pages. The first volume (THIS JOURNAL **37**, 7, 379 [1960]) deals systematically with organic compounds and reactions, the third volume (THIS JOURNAL **36**, 2, 102 [1959]) concerns special topics (dyes, polymers, etc.), and the most recent second volume carries a subtitle "Theoretical and General Organic Chemistry." The titles of individual chapters will indicate the scope of this volume: History of Organic Chemistry (35 pp.); Physical Methods (67 pp.); Bonding and Bond Types (131 pp.); Reactions and Reaction Mechanisms (135 pp.); Tautomerism (35 pp.); Intermolecular Forces and Association (48 pp.); Stereochemistry (125 pp.). Although the treatment of individual topics is quite up-to-date, there are no more than some 30 mathematical equations in the whole book and the clarity and conciseness of the style are outstanding. The separation of physico-chemical theory in this volume from the purely chemical theory in the other volumes has advantages and disadvantages. Although the present book is just a part of a more extensive treatise, it could be used separately in a similar manner to Wheland's "Advanced Organic Chemistry" or Ingold's "Structure and Mechanism in Organic Chemistry" in most graduate courses. The unique value of Klages' work, however, lies in his successful attempt to treat the whole field of organic chemistry from one point of view. Because of the rapid growth and complexity of certain highly specialized fields (polymers, small ring compounds, heterocycles, organophosphorus compounds, etc.) the type of chemists referred to as "general organic" practically disappeared and their place was taken by a variety of specialists and experts. This change, which in itself was unavoid-

(*Continued on page A236*)

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By JOSEPH I. ROUTH, Ph.D., Professor of Biochemistry, State University of Iowa, Iowa City, Iowa. About 480 pages, 6⅝″ × 9¾″, with about 277 illustrations. *New (3rd) Edition—Ready April, 1963.*

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By ABRAHAM CANTAROW, M.D., Professor of Biochemistry, Jefferson Medical College; and BERNARD SCHEPARTZ, Ph.D., Associate Professor of Biochemistry, Jefferson Medical College. 938 pages, 6½″ × 9¼″, 176 illustrations. $13.00.
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By L. JEAN BOGERT, Ph.D., formerly instructor in the Department of Medicine, University of Chicago; Instructor in Experimental Medicine, Yale University Medical School; and Lecturer in Chemistry, Connecticut Training School for Nurses, New Haven, Connecticut. About 640 pages, 6⅛″ × 9¼″, with about 204 illustrations. *New (9th) Edition—Ready May, 1963*

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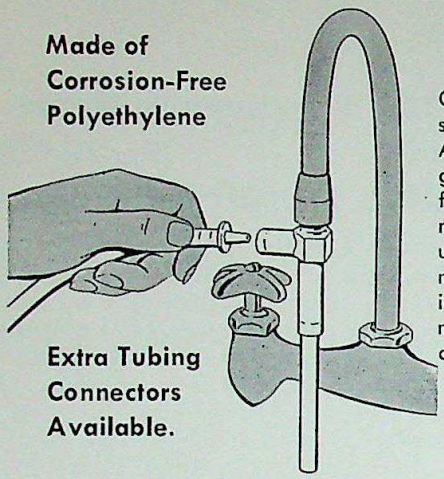
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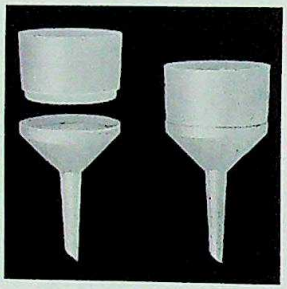
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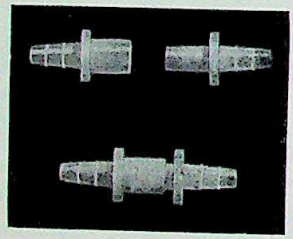
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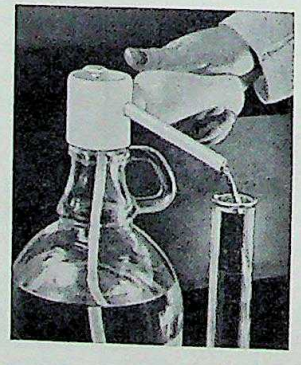
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able and necessary, was followed by a loss of perspective concerning the interrelation of the individual special fields and their common background. Professor Klages presents us just with this background which recreates the seemingly lost unity of organic chemistry. The size and scope of the work emphasizes the differences between the European and the American graduate student. It is clearly impossible to master its contents within one year and, accordingly, the European student is expected to take his most important examination toward the very end of his graduate work. The American student, on the other hand, takes his "advanced organic" just at the beginning of his graduate studies, and the final predoctoral examination requires often no more than a passing knowledge of a junior organic course. Although it is quite possible even for an average student to correlate the various graduate courses concerned with organic chemistry and thus to gain the proper perspective, it is well known to those who attend the oral doctoral examinations or who discuss chemistry with new graduates that all too often this very important breadth of view is missing. As in the previous volumes, the paper and typography are excellent and misprints are few.

ALEXEJ B. BOŘKOVEC
Pesticide Chemicals Research Branch
U. S. Department of Agriculture
Beltsville, Maryland

Index to Reviews, Symposia Volumes and Monographs in Organic Chemistry for the Period 1940–1960

Compiled and edited by *Norman Kharasch* and *Walter Wolf*, both of the University of Southern California, Los Angeles, and *Elaine C. P. Harrison*, technical editor. Pergamon Press, Ltd., Headington Hill Hall, Oxford, England, 1962. viii + 345 pp. 22 × 28.5 cm. 70 shillings.

With the burgeoning volume of chemical literature, the literature search is itself becoming a more formidable, but necessary, part of the research effort. A short cut to the literature is the presence of a good review article or monograph. But with the hundreds of review articles appearing, these, too, are difficult to find. It is, therefore, a convenience to have at one's elbow a copy of the present volume.

The titles of about seven thousand review articles taken from journals and other periodical publications, collective volumes and non-periodical publications are included. The reviews are listed by the symposia volume or journal and are cross-indexed with a total subject and an author index. In the case of *Chemical Reviews*, all of the organic papers have been listed, even those prior to 1940. A

(*Continued on page A238*)

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H. Fromherz - A. King

German-English Chemical Terminology

An Introduction to Chemistry in English and German

Fourth Revised and Enlarged Edition.
1963. xxi, 588 pp. Clothbound DM 48,00 = $12.00

The purpose of this book is to provide students, research scientists, industrial chemists and translators, having German or English as their mother tongue, with the possibility of achieving easily a detailed familarity with chemical terms and their usage in the other language. ■ This book is a comprehensive introduction to chemistry in English and German, the two texts being printed side by side on opposite pages to permit easy comparison. It attempts to indicate the meaning of terms in common use more clearly than can be done by a dictionary, by presenting each in a coherent context. Each expression which appears for the first time is printed in italics in both the English and German text, and all words designated thus will be found in the English or German index at the end of the book. In the present edition, for the first time, the index gives not only the page on which a particular term will be found, but by the addition of a letter to the page number, the position on the page — thus making it quicker and easier to find the term required. ■ The many additions have entailed a considerable enlargement of the book, whose index now contains more than 10,000 expressions as compared to the 4,000 in the first edition.

Specimen page from the English text

94 *Inorganic Chemistry*

chief commercial source is *sodium iodate*, which occurs in the Chile nitrate deposits. Iodine *volatilises* (sublimes) easily to form a violet coloured vapour. a A sensitive test for the element is the intense blue colour it gives to *starch solutions*. This reaction is the basis of *iodimetry*, a method of volumetric analysis. *Starch-iodide paper is* used as a *test- paper* for oxidising agents and is used as a *pole paper* for testing the polarity of an electric current. Iodine is a normal constituent of the human body and occurs in organic combination in the b *thyroid gland* (*thyroxin*). A 10% alcoholic solution of iodine (*tincture of iodine*) is used as a disinfectant in medicine.

c

BORON

Boron is a trivalent non-metallic element, chiefly found in combination as salts of *boric* (*boracic*) *acid*, the *borates*, in minerals, and in "*borax lakes*". *Disodium tetraborate* or *disodium heptoxotetraborate* (*borax*) $Na_2B_4O_7$ is the chief compound of this element. Fused borax readily dissolves many *metallic* d *oxides* to produce beads of characteristic colours (*borax beads*). Borax finds considerable use as a flux in *soldering*, as a *glaze* for *pottery*, for *enamels*, and, as it hinders *devitrification* in making some *optical* and hard glasses.

The element exists in both a brown, powdery amorphous form and in a e greyish black "crystalline" variety; it does not oxydise readily, but on heating in air to 700° a coating of the oxide (*diboron trioxide*, B_2O_3) as well as *boron nitride* BN is formed. Boron nitride is a *high polymer* which possesses a hexagonal, *honeycomb graphitic structure* (*inorganic graphite*). Recently boron nitride, which is *isosteric* with graphite has been transformed at high pressure f and temperature into an allotropic modification with the *diamond structure* and termed "*borazon*" or *inorganic diamond*. "Borazon" is harder than diamond and more resistant to oxygen. Boron nitride also combines with fluorine to form *boron fluoride* which gives rise to *fluoroboric acid* $H[BF_4]$ and its salts, the *fluoroborates*. *Perborates* serve as *washing powders* and *disinfectants*. g These are not true *peroxo compounds* as they lack the *peroxo-group* $-O-O-$, but *addition compounds* of hydrogen peroxide and the borates.

h

SILICON

Silicon is, after oxygen, the most abundant element in the *crust of the earth*, occurring in combination with oxygen as *silicon dioxide*, or *silica* (SiO_2) varieties of which are known as *quartz*, *flint*, *sand*, *rock crystal*, *agate*, *opal*, *kieselguhr* etc. Silica is a constituent of the many *silicate rocks*, e.g. of *granite*, i in which it occurs with *felspar* and mica. Silica is remarkably *inert* and *refractory*, even at high temperatures, and is used to make *refractory bricks* for

Corresponding page from the German text

Anorganische Chemie 95

gewonnen; aber die Hauptquelle für die Technik ist *Natriumjodat*, welches in den Lagerstätten des Chilesalpeters vorkommt. Jod *verflüchtigt* sich (sublimiert) leicht unter Bildung eines violetten Dampfes. Eine empfindliche Probe auf dieses a Element stellt die intensive Blaufärbung von *Stärkelösungen* dar. Diese Reaktion ist die Grundlage der *Jodometrie*, einer *Titrationsmethode*; *Jodstärkepapier* ist ein *Reagenspapier* für Oxydationsmittel; es wird auch als *Polreagens-* — *papier* zur Feststellung der Richtung eines elektrischen Stromes verwendet. Jod ist ein normaler Bestandteil des menschlichen Körpers und findet sich in b organischer Bindung in der *Schilddrüse* (*Thyroxin*). Eine 10%ige *alkoholische Lösung* von Jod (*Jodtinktur*) wird als Desinfektionsmittel in der Heilkunde verwendet.

BOR

Das Bor ist ein dreiwertiges Nichtmetall und findet sich hauptsächlich in c Form von Salzen der *Borsäure*, den *Boraten*, in Mineralien und in *Boraxseen*. Das *Dinatriumtetraborat*, (*Dinatrium-heptoxotetraborat*) Borax $Na_2B_4O_7$, ist die wichtigste Verbindung dieses Elements. Geschmolzener Borax löst leicht viele *Metalloxide* unter Erzeugung von charakteristisch gefärbten Perlen (*Boraxperlen*) auf. Borax findet beträchtliche Verwendung als Flußmittel beim d Löten, als *Glasur* für *Steingut*, zum *Emaillieren* eiserner Gegenstände und als Zusatz bei der Herstellung von *optischen Gläsern* und *Hartglas*; er hemmt *Entglasen*.

Das Element existiert in einer braunen, pulverförmigen *amorphen* und einer e schwärzlich-grauen „*kristallinen*" *Modifikation*; es läßt sich nicht leicht oxydieren, aber beim Erhitzen in Luft auf 700° bildet sich ein *Oxidüberzug* (*Oxidhaut*) von *Dibortrioxid* B_2O_3 und *Bornitrid* BN. Bornitrid ist *hochpolymer* und besitzt eine *wabenförmige*, hexagonale *Graphitstruktur* (*anorganischer Graphit*). Neuerdings gelang es, das mit Graphit *isostere* Bornitrid unter hohem f Druck und bei hohen Temperaturen in eine allotrope Modifikation mit *Diamantstruktur*, *Borazon*, umzuwandeln (*anorganischer Diamant*). Borazon ist härter und gegen Sauerstoff widerstandsfähiger als Diamant. Bornitrid verbindet sich mit Fluor unter Bildung von *Borfluorid*, von dem sich die *Tetrafluoroborsäure* $H[BF_4]$ und deren Salze, die *Tetrafluoroborate* ableiten. *Perborate* dienen als *Waschpulver* und *Desinfektionsmittel*. Sie sind keine echten *Peroxoverbin-* g *dungen* mit der *Peroxogruppe* $-O-O-$, sondern *Additionsprodukte* von Wasserstoffperoxid und Boraten.

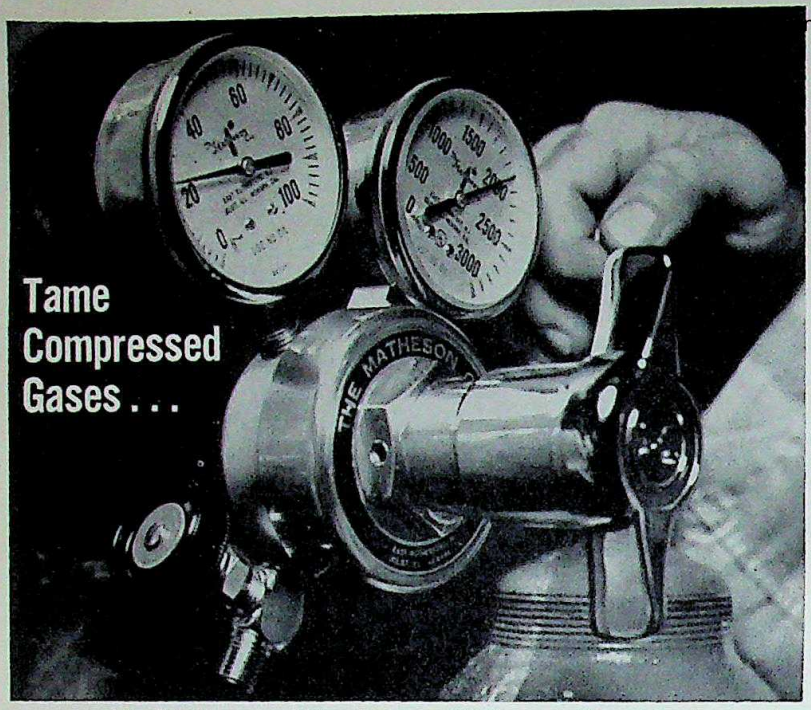
SILICIUM

Silicium ist nach Sauerstoff das häufigste Element der *Erdkruste*, wo es in h Verbindung mit Sauerstoff als *Siliciumdioxid* (SiO_2) vorkommt. Verschiedene Formen sind: *Quarz*, *Feuerstein*, *Sand*, *Bergkristall*, *Achat*, *Opal*, *Kieselgur* usw. Siliciumdioxid ist ein Bestandteil vieler *Silicatgesteine*, z. B. des *Granits*, wo es zusammen mit *Feldspat* und Glimmer vorkommt. Siliciumdioxid ist i auffallend *reaktionsträge* und *widerstandsfähig*, auch bei hohen Temperaturen, und dient zur Herstellung von *feuerfesten Backsteinen* für *Ofenauskleidungen*.

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Trevor Robinson, *University of Massachusetts*

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thoughtful help is the listing of the names and addresses of the 124 publishers.

The authors recognize certain limitations: only reviews published in English, French and German are listed. "... Many borderline books on physical chemistry, inorganic chemistry, and biochemistry—as well as some textbooks ..." are not included. Articles on the history of organic chemistry, should be included.

To test the utility of the text, randomly-chosen titles were checked: furoxans (one listing), electron spin resonance and electron resonance spectroscopy (three), Diels-Alder and Diene Synthesis (eight), Grignard Compounds and Grignard Reactions (nine), and Phosphorus Compounds (twenty-two).

This book should find its way into personal libraries of researchers, teachers, and students as a helpful, one-spot source of reviews on organic chemistry.

ERNEST I. BECKER
Polytechnic Institute of Brooklyn
Brooklyn, New York

Advances in Inorganic Chemistry and Radiochemistry, Volume 4

Edited by *H. J. Emeléus* and *A. G. Sharpe*, University Chemical Laboratory, Cambridge, England. Academic Press, Inc., New York, 1962. viii + 344 pp. Figs. and tables. 16.5 × 23.5 cm. $11.

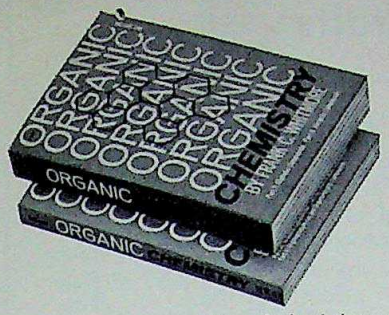
The fourth volume in this series of review articles deals with a number of interesting topics, written authoritatively and in good style: Condensed Phosphates and Arsenates, by Erich Thilo; Olefin, Acetylene and π-Allylic Complexes of Transition Metals, by R. G. Guy and B. L. Shaw; Recent Advances in the Stereochemistry of Nickel, Palladium, and Platinum, by J. R. Miller; The Chemistry of Polonium, by K. W. Bagnall; The Use of Nuclear Magnetic Resonance in Inorganic Chemistry, by E. L. Muetterties and W. D. Phillips, and Oxide Melts, by J. D. MacKenzie. The latest volume of the series is good but does not, in the opinion of this reviewer, come up to the high level set by the other previous volumes. There seems to be a tendency to move somewhat in the direction of more highly specialized topics, suggesting either that inorganic chemistry is running out of interesting broad topics, or the editors were not as astute in their selection of topics as in the past. I do not believe the former possibility for a minute.

The reviews by Muetterties and Phillips on NMR and Thilo on Condensed Phosphates and Arsenates are clearly superior, and it would be well worth while to buy this book for these two topics alone.

J. W. COBBLE
Purdue University
Lafayette, Indiana

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OXIDATION OF BROMIDE AND IODIDE IONS

Submitted by: F. B. Dutton, Michigan State University, East Lansing

Checked by: George Ferris, Haslett High School, Haslett, Michigan

PREPARATION

Prepare an acidified 0.01 *M* solution of potassium iodide and potassium bromide by adding 0.17g KI and 0.12g KBr to 5 ml concentrated HCl in 95 ml H_2O. Saturate 100 ml water with chlorine. Provide a flask or large test tube, stopper, and some carbon tetrachloride.

DEMONSTRATION

Place the halide solution and 10 ml of carbon tetrachloride in the flask, add a few drops of Cl_2 water, shake, and observe the purple color of iodine in the CCl_4. Slowly add more Cl_2 water, shaking between additions, and observe successive color changes; purple (iodine) black (iodine plus bromine), brown (iodate, colorless, plus bromine), yellow (an interhalogen compound of Br and Cl^- plus Cl_2).

REMARKS

Ask the class to explain the color changes and to compare with standard emf potentials.

$I^- \rightarrow {}^1/_2I_2 + e^-$	-0.53
$Br^- \rightarrow {}^1/_2Br_2 + e^-$	-1.07
${}^1/_2I_2 + 3H_2O \rightarrow IO_3^- + 6H^+ + 5e^-$	-1.20
$Cl^- \rightarrow {}^1/_2Cl_2 + e^-$	-1.36

These reactions have been used to test for Br^- in the presence of I^-. The process may be repeated with each halide ion separately if desired.

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DEMONSTRATION NOTES

From time to time items such as the following, which do not require a full half-page, will be listed together. Some of them will be modifications of previously published demonstrations, in which case it is suggested that they be clipped and attached to the pertinent experiment.

CORRECTION

On the December, 1962 Tested Demonstration page we misspelled the name and address of the first contributor. It should have been H. R. Tietze of Newcastle University College, New South Wales, Australia. We extend our apology.

HYDROGEN PEROXIDE

Robert H. Long of Green Mountain College, Poultney, Vt., suggests demonstrating the oxidizing action of hydrogen peroxide by adding 2 or 3 ml of a 3% solution to a solution of copper (I) chloride made by dissolving 0.5 g copper (I) oxide in 2 ml concentrated HCl and diluting with 10 ml H_2O. The development of the blue hydrated Cu (II)$^{++}$ ion indicates the oxidation of Cu (I) to Cu (II).

EDITOR'S NOTE: Adding H_2O_2 to a dilute acidified solution of $KMnO_4$ will show the reducing properties.

HELP WANTED

Several demonstrations on chromatography and on electrolysis have been received from time to time which are too long for our format or are overlapping in content. We propose to submit these to a panel to develop the best composites possible. Please send us your favorite demonstration on these topics. All contributions will be acknowledged. Address contributions to Prof. Frederic B. Dutton, Science and Mathematics Teaching Center, Michigan State University, East Lansing, Mich.

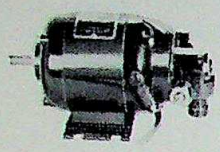
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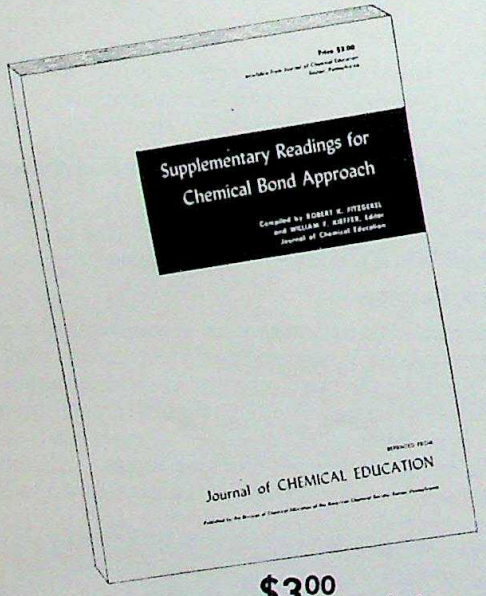
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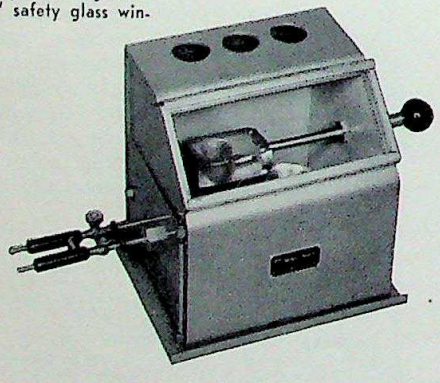
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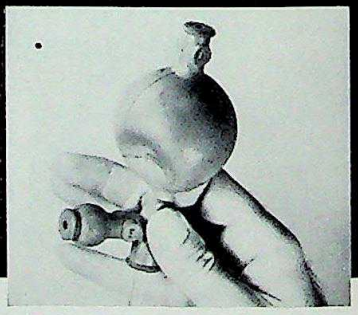
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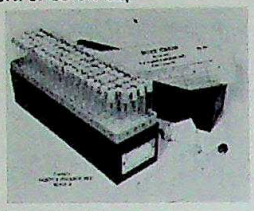
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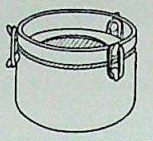


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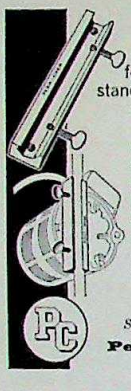
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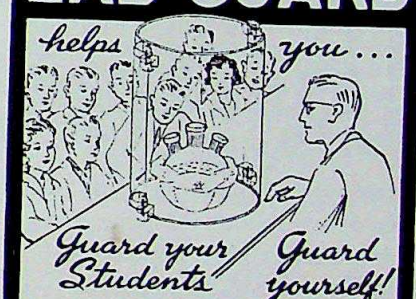
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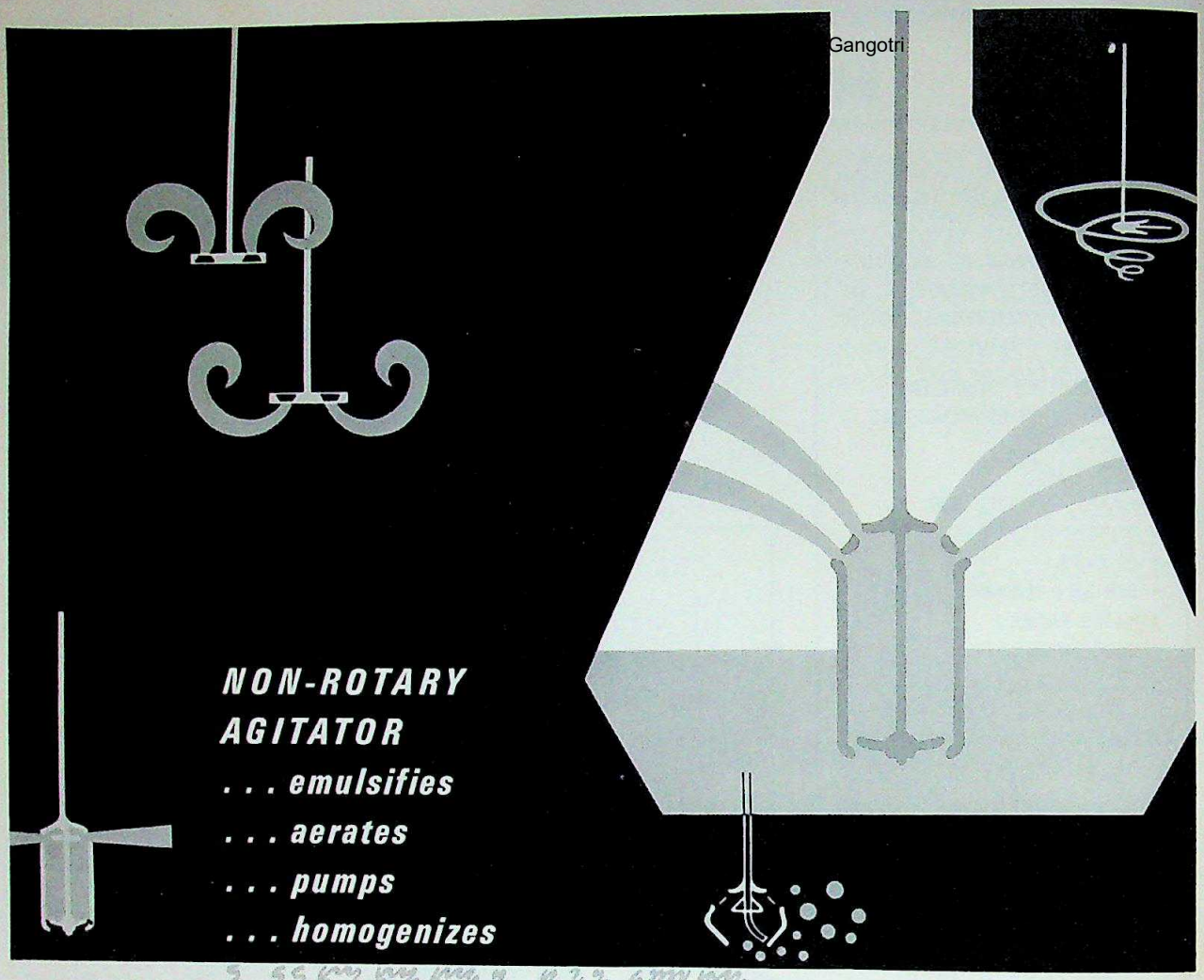
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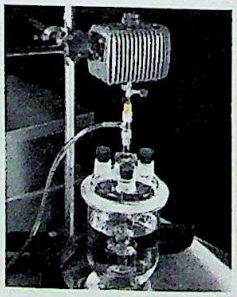


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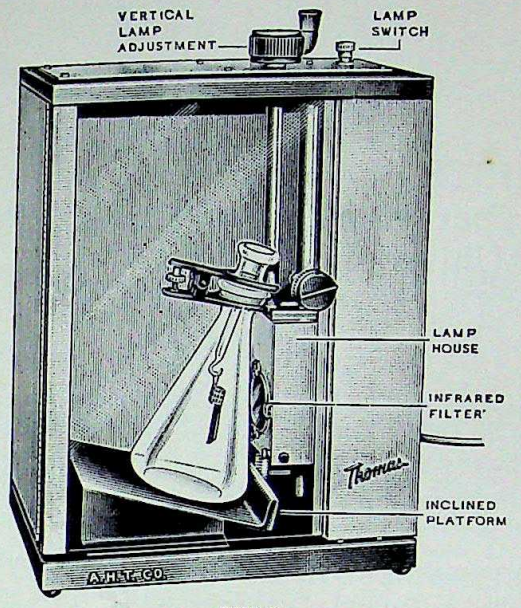
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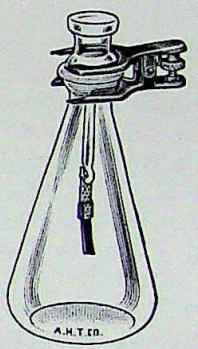
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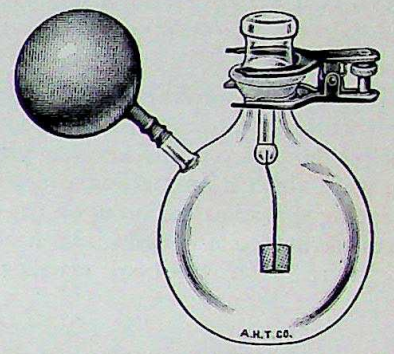
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6472-B.
Showing 6471-P10 Ogg Flask in position *(Flask not included)*



6471-P10.



6474-G10.

OXYGEN FLASK SAFETY IGNITER,* Thomas-Ogg. For combustion of organic materials in a closed oxygen flask completely shielded within a safety cabinet. Utilizes a focused infrared beam from a built-in 150-watt lamp and special black paper sample wrappers for rapid ignition in an oxygen-charged clamp-closed flask. Vertical alignment of the sample in the beam, and push-button firing are done from outside the cabinet after door is fastened.

Cabinet is of metal, 12¼ × 8 × 16 inches high overall, with transparent acrylic plastic door with full-length hinge, baffled vents and spring-loaded latch. Lamp is mounted in housing with screw crank elevating device; fixed focusing reflector is sealed within lamp envelope. Inclined platform tilts flask to bring sample close to lamp. Flask can be adjusted from front to rear from outside cabinet.

Designed for use with Thomas-Ogg combustion Flask, but accommodates any flask up to 2000 ml, such as Thomas-Lisk, in which stopper can be clamped securely.

6472-B. Safety Igniter, Thomas-Ogg, as described, with flask platform, infrared filter, 100 black paper sample wrappers, extra lamp bulb, 3-wire cord, 3-prong plug with adapter and directions for use, but without combustion flask. For 115 volts **155.00**

OXYGEN COMBUSTION FLASKS,* Thomas-Ogg, of borosilicate glass, conical, designed especially for use in Ogg Safety Igniter but can also be used separately. Mouth is formed by socket of spherical joint 35/25, and stopper fabricated from matching ball member. Stopper has extension with hook for suspending the detachable sample carrier. Carrier is of perforated platinum sheet 1¾ inches long × ⅜-inch wide. Stopper is held securely during combustion by Thomas Pinch Clamp and can be tilted to permit easy release of vacuum following combustion.

6471-P10. Oxygen Flask, Thomas-Ogg, as described, 500 ml capacity, complete with stopper, clamp and platinum sample carrier, but without sample wrappers **41.70**
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6474-G10. Oxygen Flask, Thomas-Lisk, as described, round bottom, 1000 ml capacity, complete with stopper, clamp and 144 rubber balloons, but without sample wrappers . . **54.20**
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*Patent applied for. Based on developments by Clyde L. Ogg and associates, Eastern Utilization Research and Development Division, A.R.S., U.S.D.A., Philadelphia, Pa. Described at the International Symposium on Microchemical Techniques, August, 1961.

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Edited by **S. Z. LEWIN,** New York University, New York 3, N. Y.

These articles, most of which are to be contributed by guest authors, are intended to serve the readers of this JOURNAL *by calling attention to new developments in the theory, design, or availability of chemical laboratory instrumentation, or by presenting useful insights and explanations of topics that are of practical importance to those who use, or teach the use of, modern instrumentation and instrumental techniques.*

VIII. Instrumentation for Particle Size Analysis. Part One

S. Z. Lewin, *Department of Chemistry,* New York University

The counting and classification according to size of the particles in a valid sample of a powdered material represents one of the most difficult of all measurement techniques. When the particle sizes extend down into the micron and fractional micron ranges, the experimental difficulties resulting from the large number of individual particles that must be included in the sample in order to give a statistically reliable, representative result, and the tendency toward agglomeration of small particles into clusters, combine to make this type of measurement tedious, time-consuming, and expensive at best, and imprecise and inaccurate at worst. However, many of the most important properties of solids are related to the distribution of particle sizes in the system, and the need for effective, practical means of obtaining such information has spurred the development of a number of instrumental approaches to particle size analysis.

The distribution of particle sizes is of critical importance in the behavior of catalysts, cements, ceramic compositions, pigments, insecticides, grains and food products, pharmaceuticals, plastics, explosives, fuels, adsorbents, and numerous other products of the greatest economic importance. In addition, increasing attention is currently being paid to the measurement and monitoring of the particle concentrations and size distributions of aerosol suspensions in connection with the control of air pollution, as well as in the maintenance of the so-called "white areas" or "clean rooms" in industries where components of such precise dimensions are produced that air-borne particulates must be scrupulously controlled. Finally, particle counting and sizing has long been, and continues to be, of major importance in medical and clinical work.

Types of Particle Size Analyzers

Three fundamentally different approaches are commonly employed in the determination of particle size distributions. One group of techniques is based upon the *discrete counting and mensuration of the individual particles* in the sample. In this case, the sample must be dispersed sufficiently to permit the individual particles to be sensed separately, and each particle must be measured in turn. The problem of dispersing the specimen so that all agglomerates are broken down into the individual particles, without at the same time breaking up the individual particles themselves is a difficult one, and in most cases it is not possible to say when the first process has been completed or when the second has commenced. In addition, a large number of particles must be counted and measured in order to yield a statistically significant result, and if this is done visually by an operator, the technique requires very great patience, and not inconsiderable skill. Complex and expensive instrumentation is now available for replacing the human observer by an electronic scanner. However, if the majority of the particle sizes in the sample are of the order of magnitude of a few microns in diameter, the counting and measuring of several million particles may correspond to a total sample weight of the order of only a few milligrams. The problem of selecting such a small sample from a large batch of material and insuring that it will be truly representative of the total batch is a formidable one indeed.

A second approach to particle size analysis is based upon *fractionation into predetermined size ranges,* and measurement of the weight or volume of these fractions. Here, too, the sample must be thoroughly dispersed, and the physical properties of the particles are employed to create a separation according to size. Thus, sieves with controlled mesh dimensions permit particles smaller than the hole size to pass through, while larger sizes are retained. Alternatively, the different rates of fall of particles of different sizes through a fluid medium may be employed as the agency producing a separation and segregation of the particles. The fractionation techniques have the advantage of being more convenient and rapid than the methods based on discrete counting, and the former may utilize quite large samples, so that the problem of the selection of a representative sample is not a limiting factor in the final results. However, fractionation tends to give less detailed and precise information about the distribution of particle sizes than is possible with direct observation of individual particles. Also, there is often considerable difficulty in achieving an adequately stable dispersion of the sample without producing considerable attrition of the particles, thereby materially altering the particle size distribution to be measured.

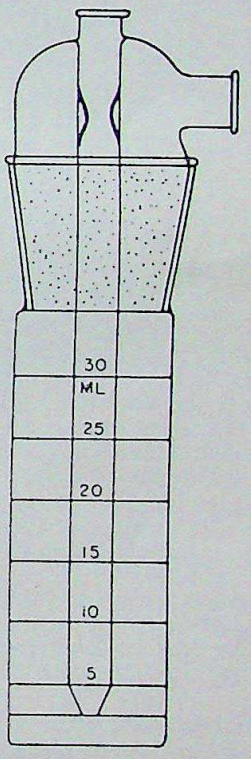


Figure 1. Impinger of Gelman Instrument Co. for dust sampling. Entrance tube is constricted to increase the velocity of the air stream and cause particles to be trapped at the bottom of the tube because of inertia. A small amount of liquid at the bottom prevents the particles from being lost in the effluent stream.

The third approach involves the application of a technique based upon the *measurement of a particle-size-dependent integral property* of the powder. Certain over-all properties of a sample can be related to the number and sizes of the particles present in a given volume or weight, and the measurement of these properties can, in principle, be interpreted in terms of the particle size distribution. Thus, e.g., the resistance to the flow of air

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through a standard thickness of a sample compacted in a standard way is a function of the particle size distribution in the sample. Other properties that are utilized to provide information on particle sizes include: the scattering of light, X-rays, or nuclear radiations; adsorption onto the surfaces of the particles of dyestuffs or gases; heat of reaction; thermal conductivity; rate of reaction or dissolution. This type of approach generally yields the least insight into the distribution of particle sizes, for it is usually the case that many different distributions can lead to the same integral value of the measured parameter. This type of technique can be, however, very valuable as a means of obtaining rapid information concerning the *average* particle size (or, alternatively,

(*Continued on page A260*)

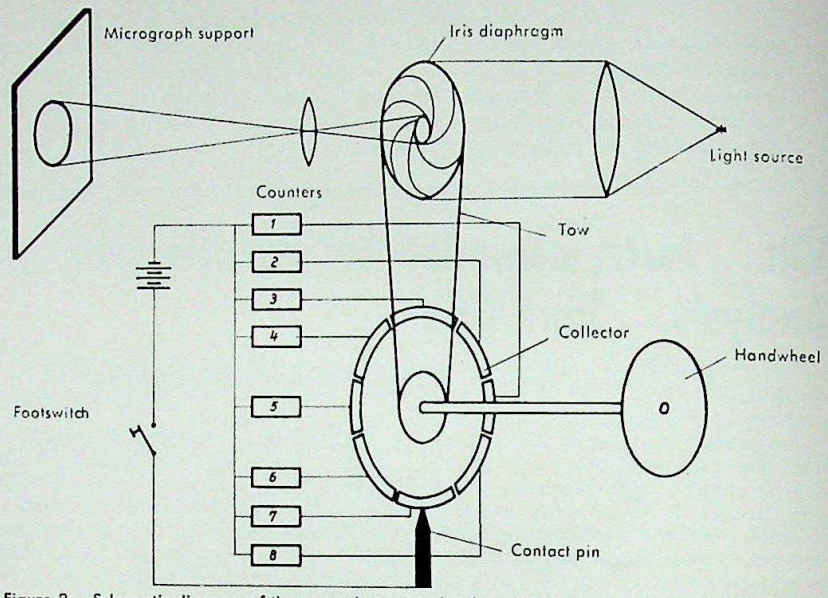


Figure 2. Schematic diagram of the operating principle of the Carl Zeiss Particle Size Ana'yzer.

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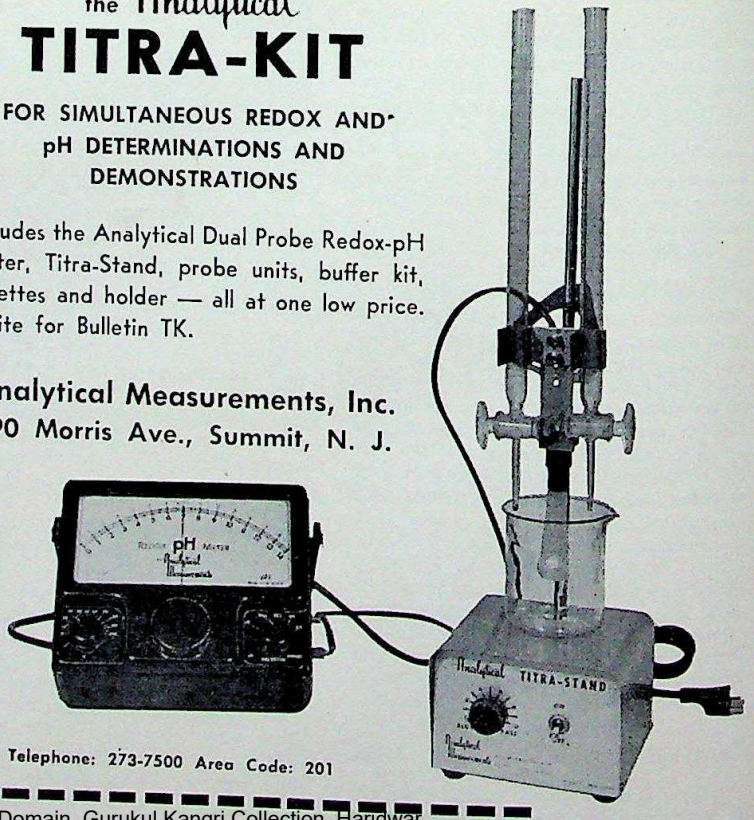
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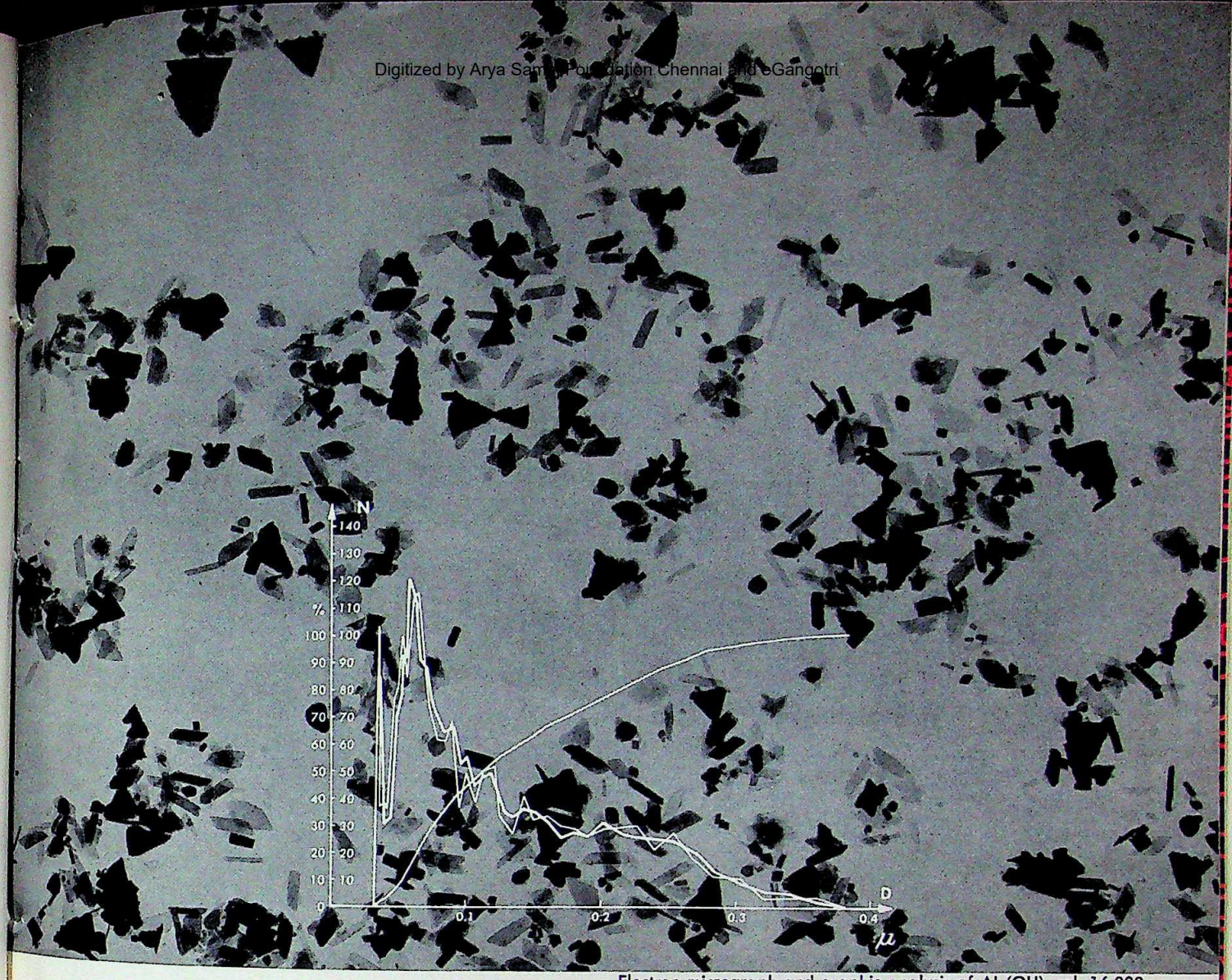
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Electron micrograph and graphic analysis of AL $(OH)_3$ sol. 16,000x.

How to get an accurate picture of particle size distribution quickly

The Carl Zeiss Particle Size Analyzer TGZ3 is basically a combination projector and electrical counting device. It is easy to operate: Place the enlarged photomicrograph or electron micrograph on the stage of the instrument. Turn a knob until the round, bright spot of light has the same area as the selected particle. Then press a foot pedal. A signal pulses to one of the 48 counters, determined by the size of the image of the iris diaphragm forming the spot. At the same time a punch descends and puts a minute hole in the counted particle to prevent repetition of a count.

With this instrument you can count and classify approximately 1000 particles in less than 15 minutes. Fatigue is reduced and accuracy improved.

The circular shape of the bright spot makes it easy to estimate sizes, also length and width of rod-shaped particles. Step widths can be recorded as absolutely constant or exponentially increasing and as either a distribution or summation curve.



The Analyzer is about the size and weight of a typewriter. It offers two particle-image measuring ranges: 1.0 to 9.2mm and 1.2 to 27.7mm. Since it is semi-automatic you can also count agglomerations of particles. A knob allows you to adjust background light for comfortable contrast. Fields in which this instrument is successfully used are: rubber, pigments, films, abrasives, etc. Write to us for further details. **Complete service facilities available.**

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the average size of the inter-particle spaces).

The continually growing need for information on particle sizes in research and industry has stimulated instrument manufacturers to develop a number of practical devices for this purpose. The design and characteristics of these commercially available instruments are summarized below.

Discrete Counting Techniques

The simplest approach to particle size analysis involves the use of a microscope for the visual observation of a sample which has been spread out on a glass slide, or of a filter that has been used to catch aerosol particles. A line of sampling devices for trapping out particles suspended in air or liquids is made by the Gelman Instrument Co., Chelsea, Michigan; an example of an impinger used for catching dust particles in a layer of liquid at the bottom of a tube is illustrated in Figure 1 (Type M-1, $7.50).

Visual Area Estimation

A device that facilitates the counting and sizing of the particles seen through a microscope is the Carl Zeiss Particle Size Analyzer (Model TGZ-3, $2860), of Carl Zeiss Inc., New York 17, N. Y. The principle of this device is illustrated in Figure 2. A photomicrograph is obtained of the field on view seen through the microscope, and this photograph is positioned on an illuminated viewer plate. A particle is selected and centered, and by means of a handwheel, an iris diaphragm is opened or closed until the area of its opening approximates the area of the

(*Continued on page A262*)

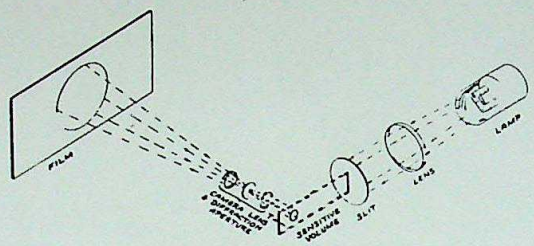
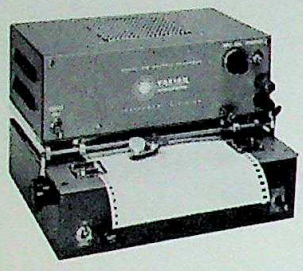


Figure 3. Optical lay-out of the Royco Aerosol Camera. Particles drawn into the sensitive volume of the camera, either in a free air stream or by impaction onto a clear glass plate located there, are illuminated at right angles to the plane of the film. The light scattered by the particles produces magnified images of the particles.

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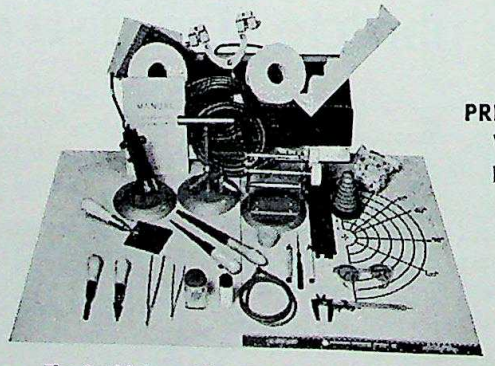
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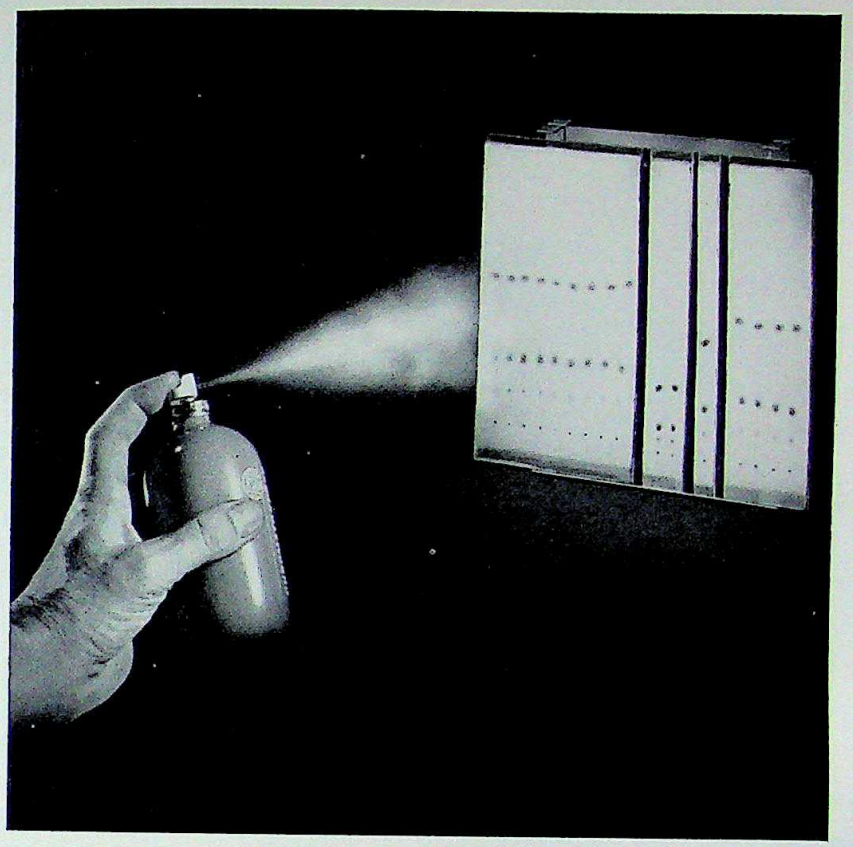
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particle. A tool-driven stylus then moves, causing a digital counter corresponding to the diaphragm size to advance one unit, while a small hole is simultaneously punched through the photograph to show that the particle at that location has already been measured and counted. About 1000 particles can be measured in fifteen minutes, and the particle sizes are recorded in 48 categories. The range of particle sizes on the photograph may be from 1.0 to 27.7 mm; the actual particle sizes that these dimensions correspond to in the specimen depend upon the degree of magnification used in obtaining the photomicrograph.

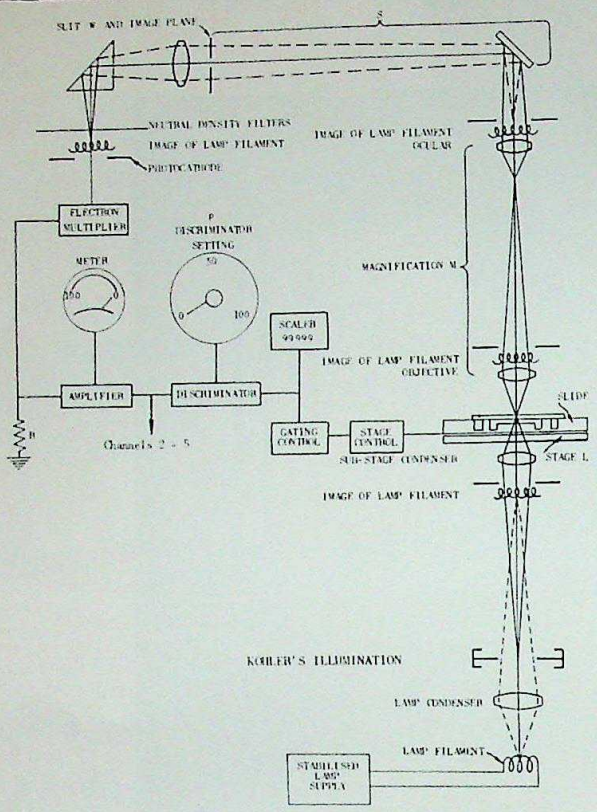


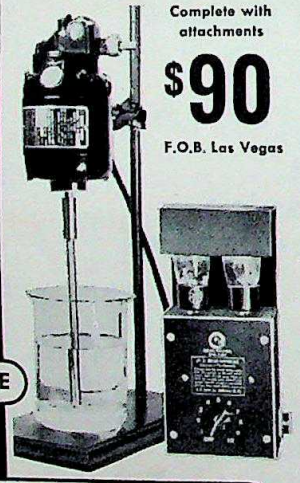
Figure 4. Design principle of the Casella Automatic Particle Counter and Sizer.

Aerosol Camera

Photographic recording for subsequent measurement of the particles in an aerosol is the basis of the design of the Aerosol Camera ($1050) made by Royco Instruments, Inc., Palo Alto, California. This camera provides for the illumination of the particles at right angles to the plane of the photographic film, as illustrated in Figure 3. The particles produce images on the film that are magnified by 25 to 60 times, due in part to the optical lens system, and in part to the Fraunhofer diffraction pattern produced about each particle. The camera weighs 8 pounds, and can be powered by batteries, or by line voltage. Particles in the range from 2 to 60 microns can be measured to ±2 microns. If the aerosol concentration is below 900 particles per cubic centimeter, the air stream may be impinged on a clear window in order to trap out and concentrate the particles prior to photographing them.

(*Continued on page A264*)

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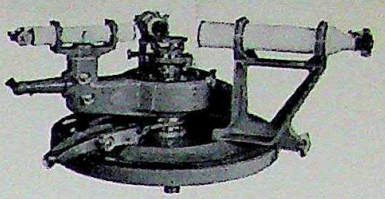
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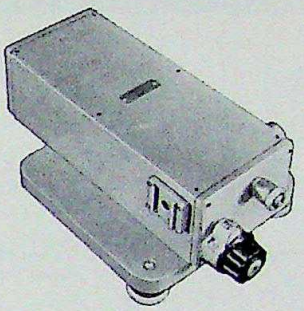
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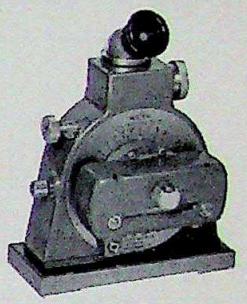
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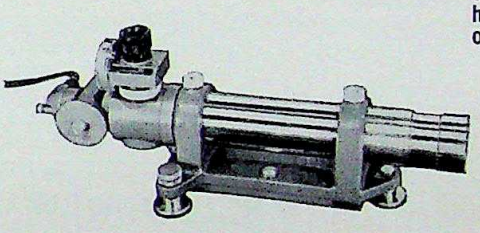
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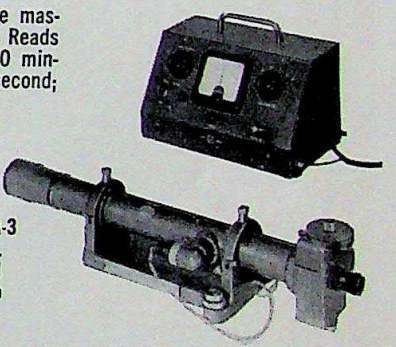
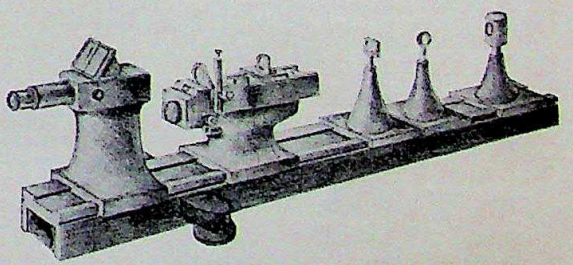


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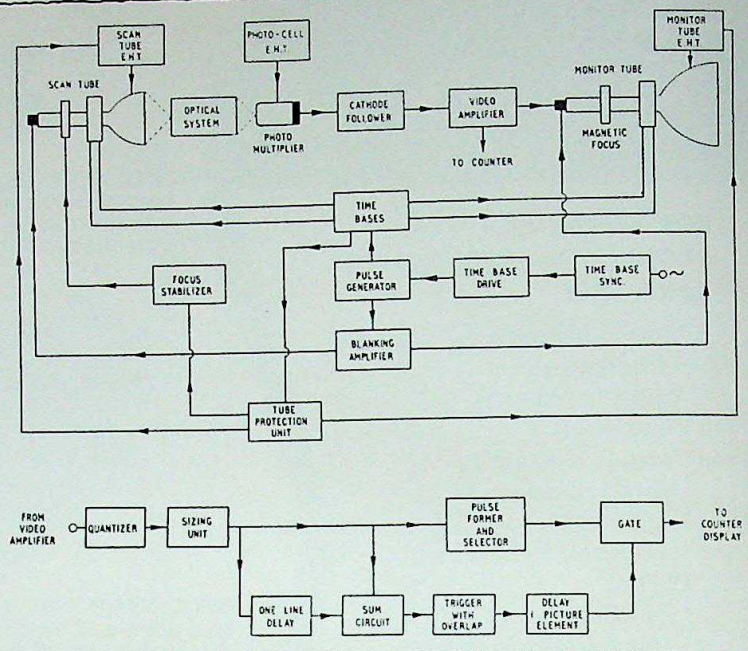


Figure 5. Block diagram of the design principle of the Cintel Flying-Spot Particle Resolver.

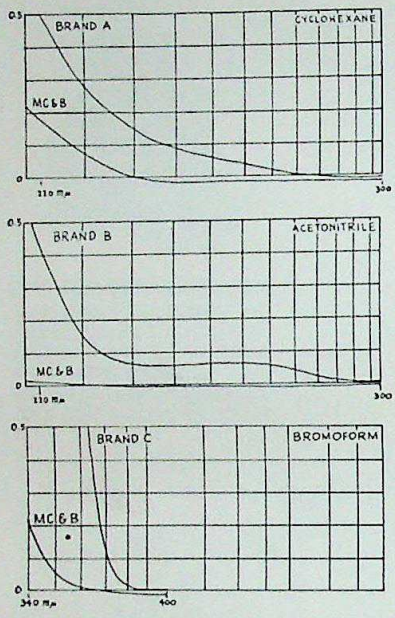
Oscillating Microscope Stage Scanner

Completely automated counting and measuring of individual particles spread out on a glass slide is accomplished in the Automatic Particle Counter and Sizer made by Casella, Ltd., London, England

ment $6235, five channel model, $12,000). The design principle of this instrument is shown in Figure 4. The sample is dispersed on a standard 3 × 1-inch microscope slide, and placed on a stage that is driven by an oscillating motor in such a

(Continued on page A266)

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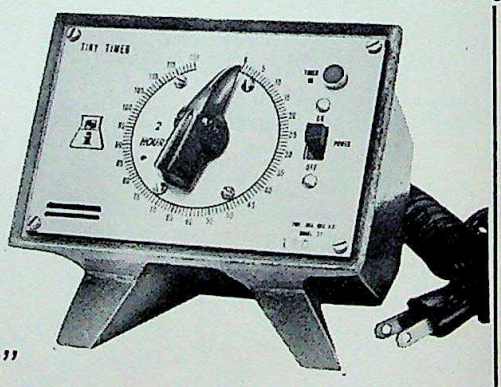
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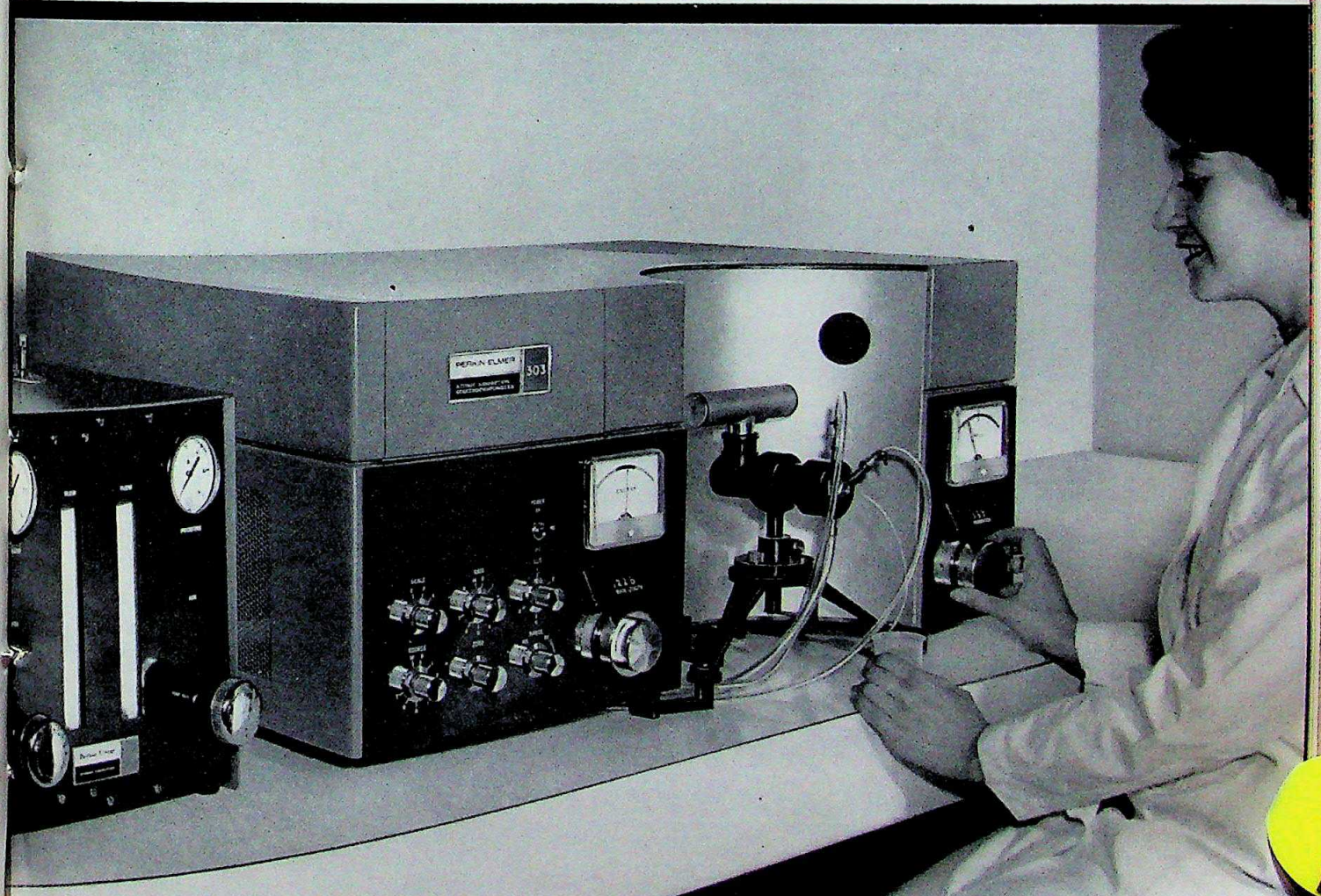
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Mercury ⊙ Molybdenum ⊙ Nickel ⊙ Palladium ⊙ Platinum ⊙ Potassium ⊙ Rhodium ⊙ Rubidium ⊙ Selenium
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To meet the need for an easy-to-operate atomic absorption spectrophotometer suited to general laboratory use in analyses of metallic trace elements, Perkin-Elmer presents the new Model 303. Designed around the principle of absorption by ground-state atoms of the resonance line of a lamp having a cathode of the metal being sought, the instrument is highly sensitive—detects concentrations ranging below one ppm for most metals. It is capable of producing, in less than 4 minutes, including set-up time, many analyses that take 2 to 3 *days* by wet chemistry. Applications include determination of magnesium, calcium, potassium, sodium and trace metals in blood, urine and tissue samples; magnesium, zinc and lead content in ferrous, aluminum and copper alloys; trace metals in plants and animals; metal components in process streams; and changes in metals content of lubricating oils, as a check on engine performance.

For complete Model 303 specifications write to Instrument Division, Perkin-Elmer Corporation, 870 Main Avenue, Norwalk, Connecticut.



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fashion that the stage is caused to advance a distance of 0.05 mm as it oscillates from left to right through a distance of 10 mm. The stage advances a total distance of 5 mm while making 100 of these side-to-side traverses; then its direction of advance reverses, and it returns to the starting position while making another 100 traverses. Thus, an area of 5 mm × 10 mm is scanned in 200 passes during a complete run. A variable slit with openings as small as 0.3 microns passes a portion of the field of view of the microscope to a photomultiplier tube. The pulses seen by the latter are amplified, classified according to amplitude, and totalized in the electronic circuitry. The count recorded in each channel is a function of the slit width and the number and sizes of the particles. By making measurements with several different slit widths, it is possible to obtain data that can be analyzed mathematically to yield the particle size distribution. This instrument is designed for particle sizes in the range from 1 to 200 microns.

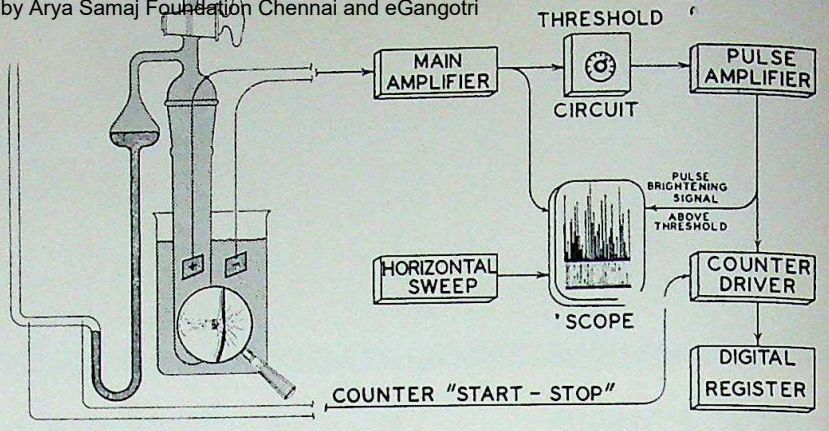


Figure 6. Design principle of the Coulter Counter. Mercury flowing along the glass tube at left activates the start and stop circuits. Fluctuations in electrolytic conductivity caused by particles passing through the micro orifice are fed to the main amplifier.

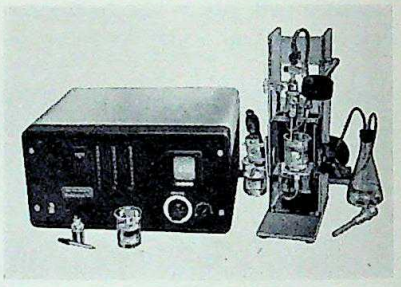


Figure 7. Complete set-up of the Model A Coulter Counter.

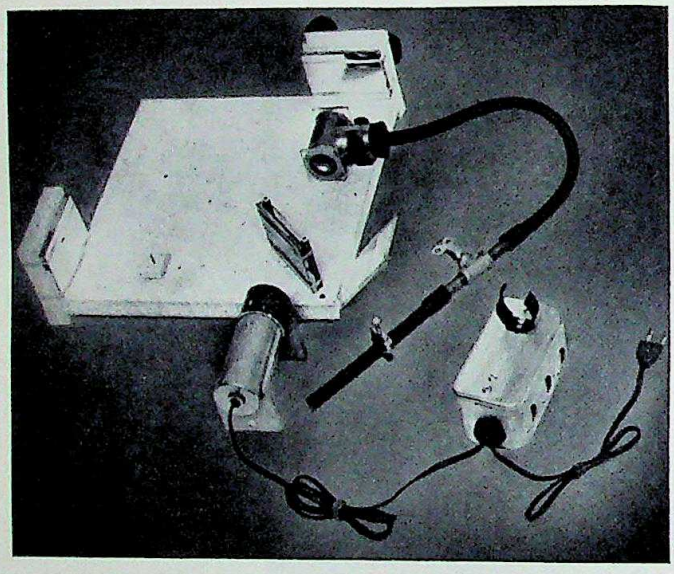
Light Spot Scanner

Another approach to an automated particle counter is embodied in the Flying Spot Particle Resolver made by Rank Cintel Limited, London, England (available in the U.S. through Instrument Corporation of America, Baltimore 18, Maryland; $22,000). In this case, the scanning of the sample is accomplished by means of a light spot produced by the effect of an electron beam on a fluorescent screen (similar to the principle by which a curve is traced on the screen of an oscilloscope). The design of this instrument is shown in diagrammatic form in Figure 5. The light passing through the slide on which the sample is spread is modulated in intensity in accordance with the density and shape of the particles, and these effects are sensed by a photomultiplier tube. An output signal is fed to a video amplifier, which can present an image of the sample on a monitor cathode-ray tube. For particle sizing, an electronic circuit is used which creates pulses of selectable width corresponding to any desired particle size on the slide. All particles less than this size produce pulses which are smaller than the reference pulses, and are

(Continued on page A268)

New ESI-approved

MICHELSON INTERFEROMETER



MSC Catalog No. 3500 Michelson Interferometer for use in the PSSC Advanced Topics program. This is a high-quality, fundamental measuring instrument using the interference between light waves as the standard of length. This new instrument is easily adjusted and combines the qualities of simplicity and rugged construction. Now, with Macalaster Scientific's new student Interferometer and cell unit, one can successfully measure the index of refraction of air to five decimal places. Completely assembled. PRICE . $20.00
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not counted. Thus, in a given scan, the total count will correspond to the total number of particles larger than a selected size. By means of successive scans with different reference pulse amplitudes, the size distribution function can be derived. Particles between 1 and 160 microns in dimensions can be sized and counted in this way. Resolution of the visual presentation on the 8 × 8-inch monitor screen is 0.1 micron.

Electrolytic Conductance Pulse Counting

An instrument is available that counts and sizes individual particles dispersed and suspended in a liquid medium, rather than on a glass slide as in the instances just described. It is the Coulter Counter, made by Coulter Electronics Inc., Chicago 14, Illinois (Model A, $6000). The sample is put into suspension in an electrolytically conductive liquid, and is caused by the movement of a mercury piston to flow at a constant velocity through an orifice of selected diameter. As indicated in Figure 6, the movement of the mercury column in its containing tube closes electrical circuits that initiate the count, and subsequently stop it. During the counting cycle, the passage of a suspended particle into the orifice causes the effective resistance between the sensing electrodes to increase, and an electrical pulse is fed to the amplifier. The magnitudes of the pulses are a function of the volume of the particles relative to the area of the orifice, and pulse height selection circuitry is employed to permit registration of the numbers of pulses having amplitudes in excess of various selected threshold values. Apertures from 30 to 200 microns in diameter are used to count particles ranging from 0.7 to 150 microns. A given aperture permits particle sizes spanning a 20 to 1 range to be detected. The start and stop contacts are separated by a distance that corresponds to 0.5 cc, and this volume passes through the aperture in 10 to 15 seconds. The particle concentration may be as high as 1 million per milliliter; the suspension liquid must disperse the sample completely, and agglomeration should be prevented during the time needed for completion of a run. It may be necessary to add surface-active agents to produce a sufficiently stable dispersion. The complete instrumentation of the Model A is shown in Figure 7. A Model C is available that provides simultaneous read-out of up to 12 different size levels.

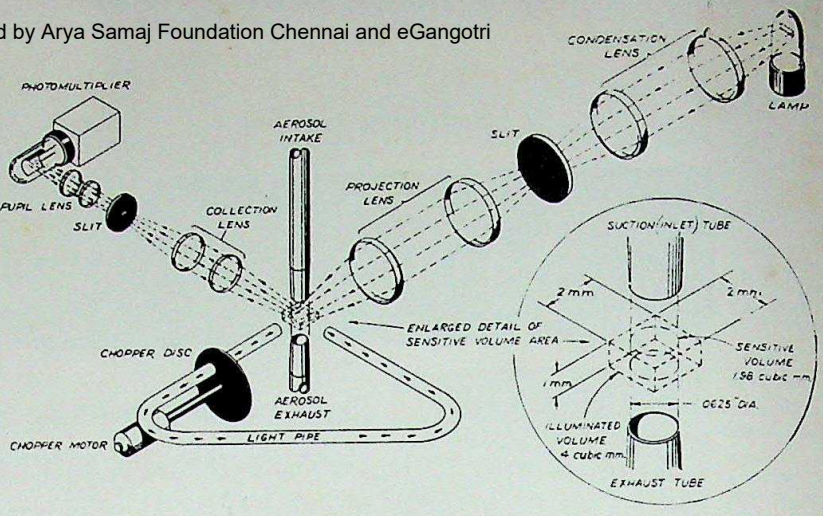
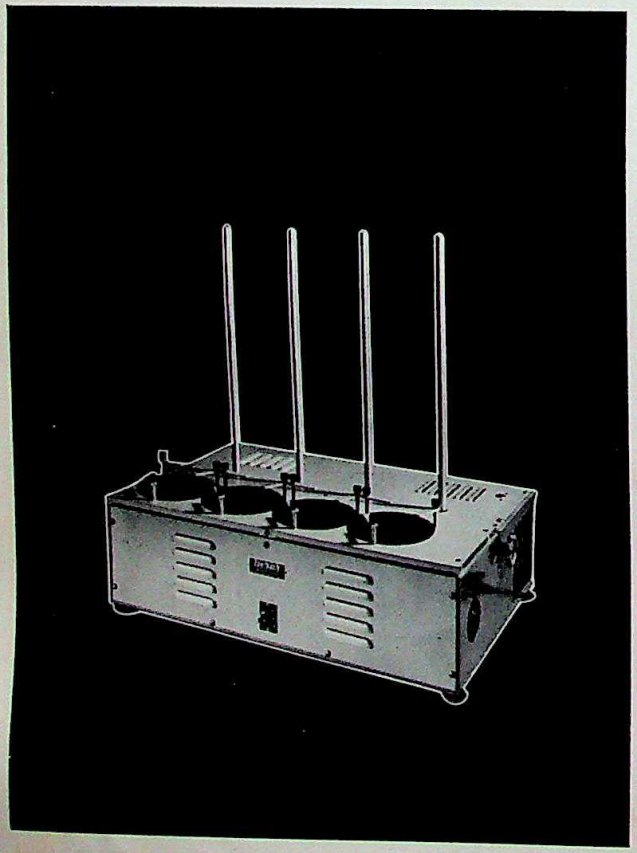


Figure 8. Design principle of the optical system of the Royco Instruments line of air-borne particle monitors.

Scattered Light Particle Counters

A series of instruments for the moni-

(*Continued on page A273*)



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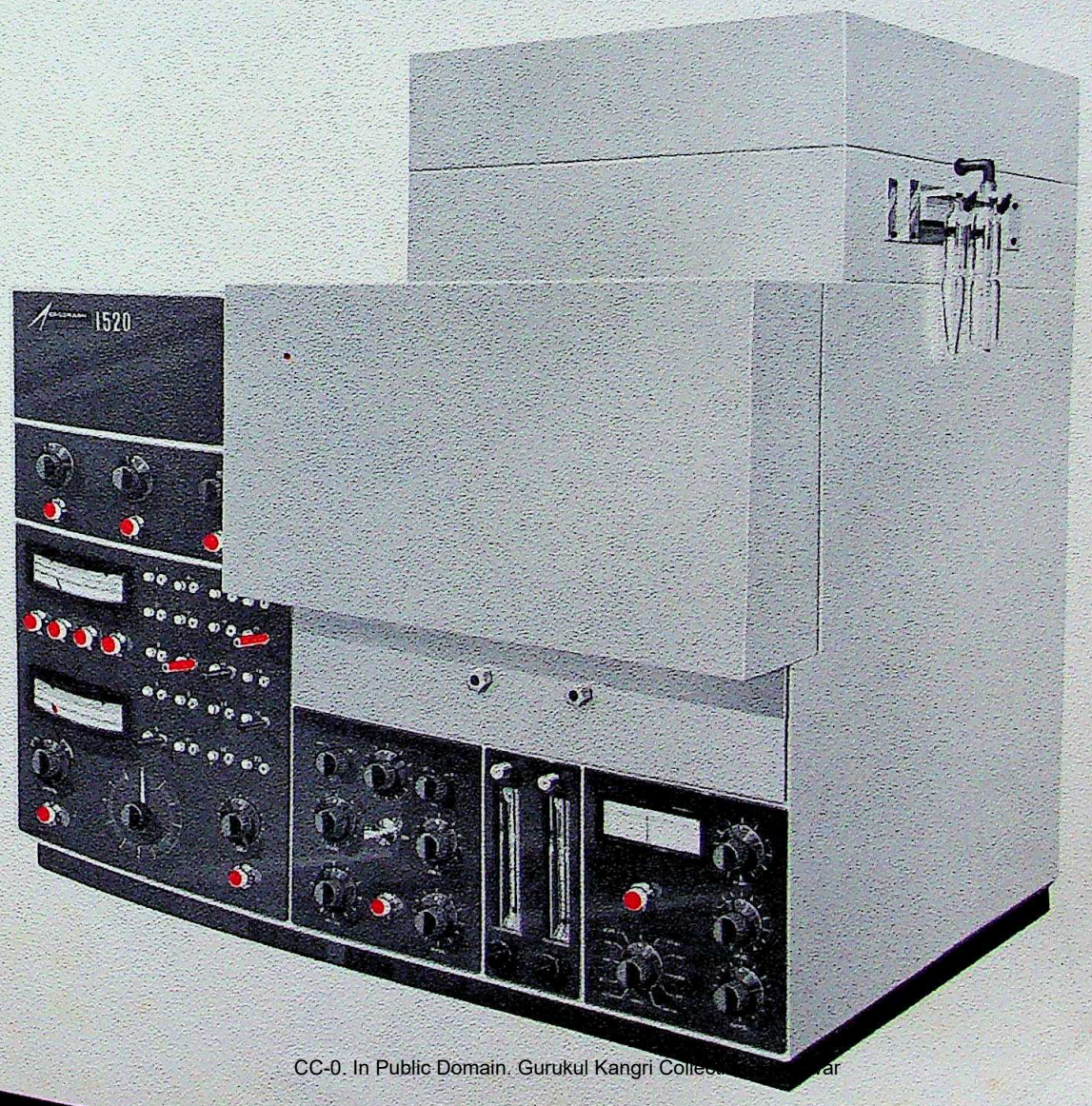
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In addition the 1520 is a deluxe preparative unit with on-column or flash vaporized injections capable of using up to 40' x 3/8" columns. Collection is made with Autoprep bottles held in a two-position mechanical changer.

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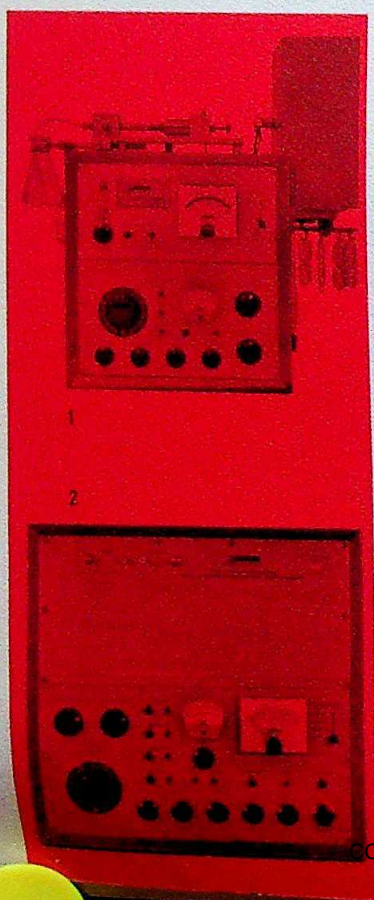
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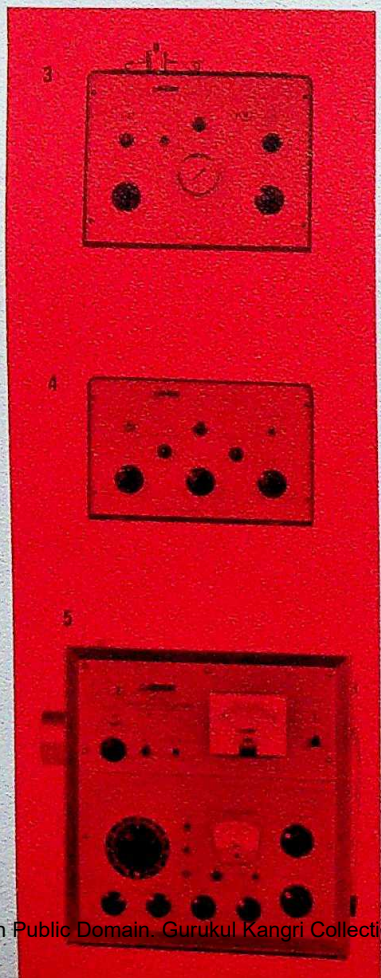
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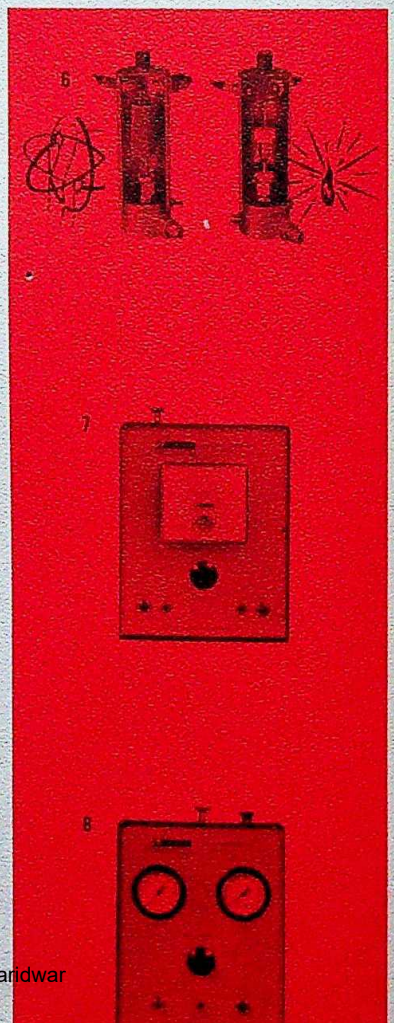
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is a manual temperature programming chromatograph with separate heaters for column oven, detector oven, and injector; with indicating pyrometer, air circulating fan, transistorized power supply. Price **$1085**



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with filtered air supply is complete with meter, controls, plumbing and ⅛" compression fittings for hydrogen and air connections. Especially designed for use with Flame Ionization Detectors. Price **$295**

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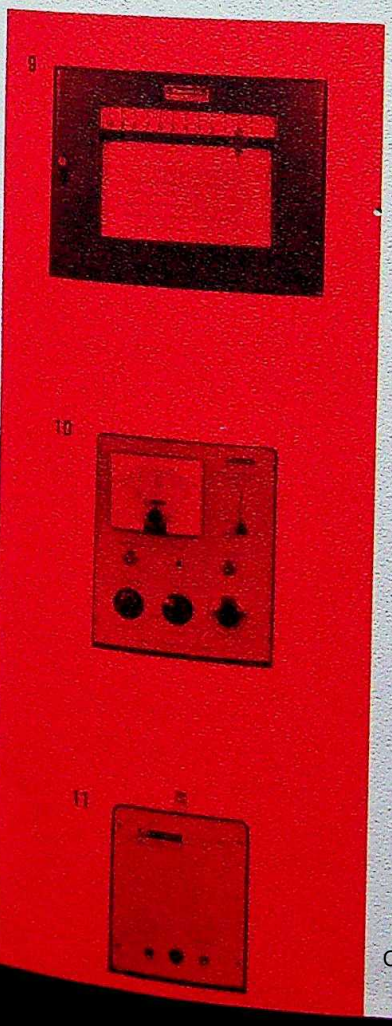
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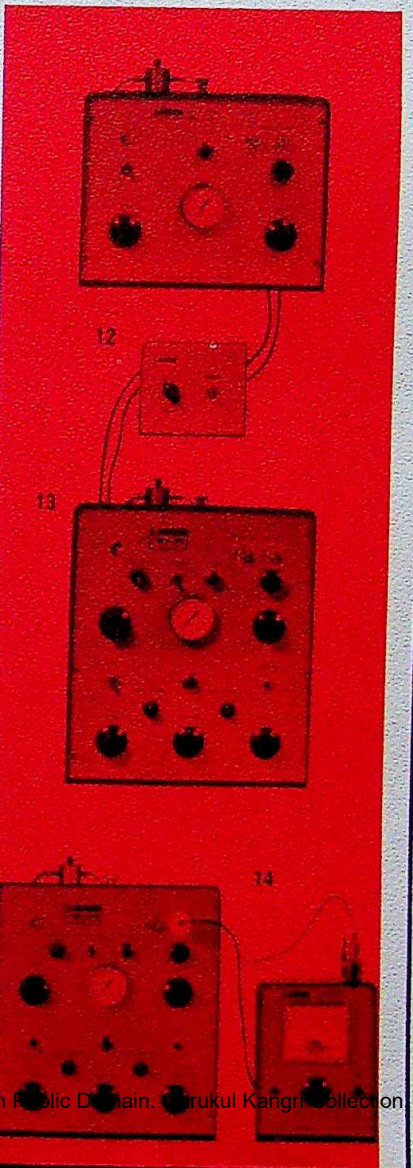
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toring of air-borne particulates by automatic counting and sizing is made by Royco Instruments, Palo Alto, California. These are based upon the optical arrangement illustrated in Figure 8. Light from a tungsten filament lamp is focused by means of a condenser lens system onto a 1 × 2-mm slit, in order to define the beam, and block out extraneous light. The light diverging from this slit is focused by means of a projection lens onto the air stream, which continuously flows through the instrument. The light beam is finally caught in a light trap and absorbed.

Light scattered from particles in the air stream is focused onto a photomultiplier detector, producing pulses the magnitudes of which are proportional to the particle size. A copper-clad Lucite light-pipe is employed to feed chopped pulses of the incident beam back into the system in a manner which enables the phototube to detect them. These pulses are formed by holes in a rotating disc located directly behind the light-trap. The pulses are used to provide a known amplitude and frequency of signals for calibration of the optics and electronics of the instrument.

The flow through the device of the air stream being sampled is designed to produce laminar flow at a velocity that causes particles to enter the viewing region one at a time. With a transit time of $\frac{1}{3}$ millisecond per particle, aerosol concentrations up to 20 million particles per cubic foot can be admitted without significant errors occurring due to coincidence losses. The electronic circuitry of the Model PC 200A Particle Counter ($7500) is shown in block diagram in Figure 9. Particle size readings can be programmed over any desired combination of 16 ranges from 0.3 to 10.0 microns, for counting intervals from 0.3 to 10 minutes.

A convenient instrument for the calibration of aerosol particle monitors is the Model 255/6 Aerosol Generator ($890), the design of which is indicated in Figure 10. This instrument produces a stable aerosol of spherical polystyrene latex particles of known size, over the range of 0.1 to 5 microns.

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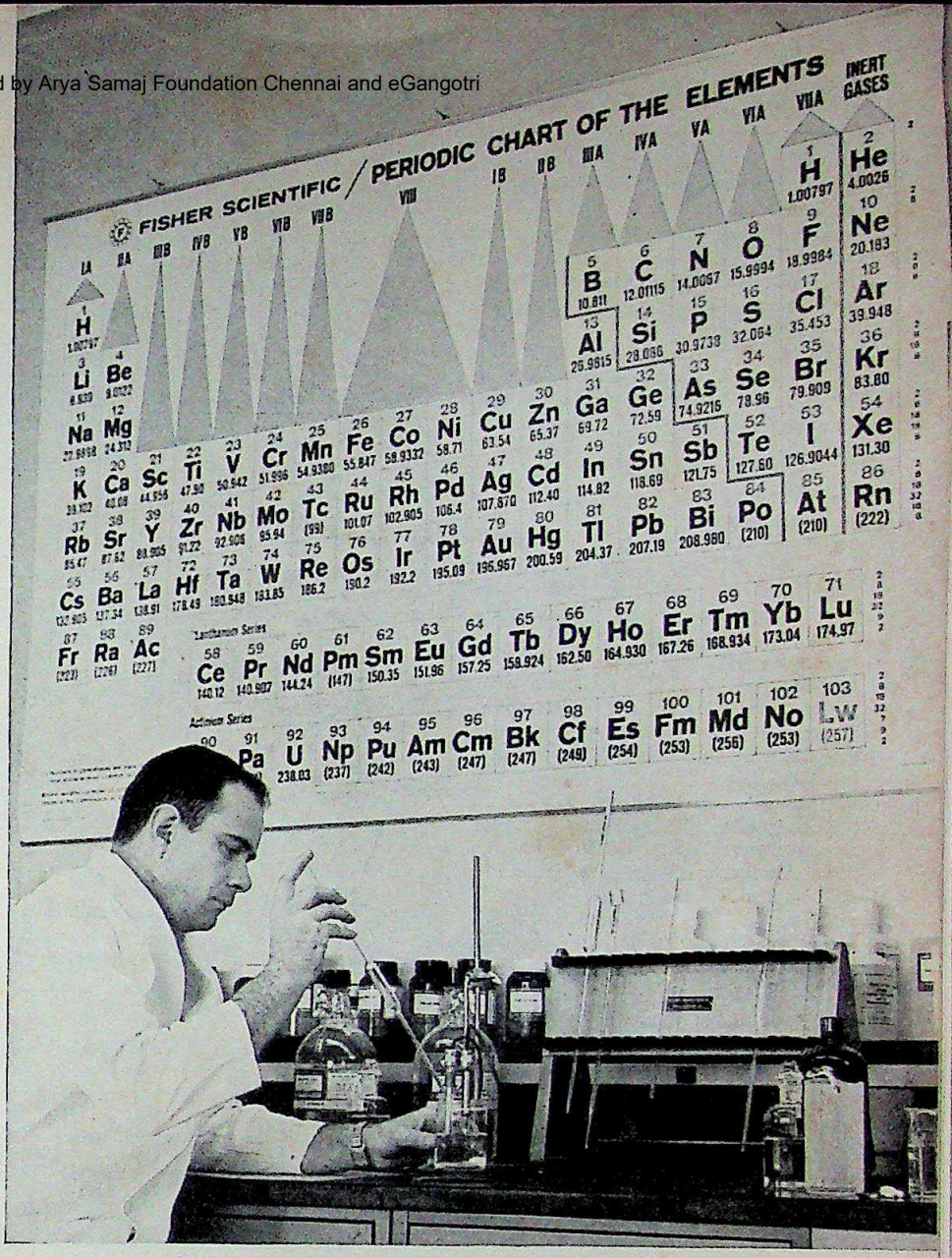
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Next: Conclusion of the survey of particle size analysis instrumentation.

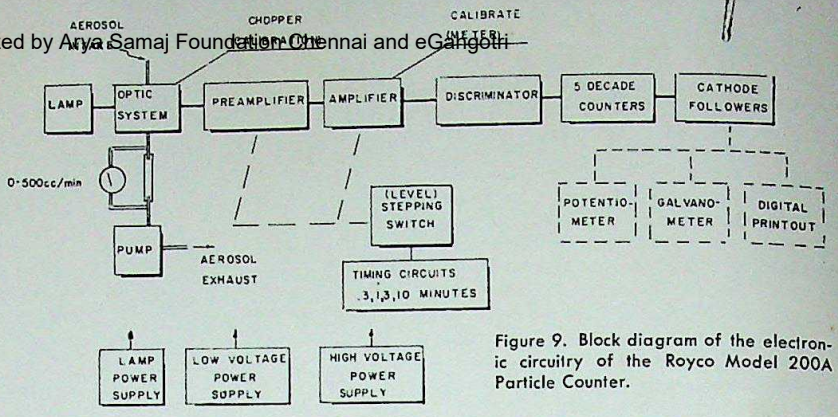


Figure 9. Block diagram of the electronic circuitry of the Royco Model 200A Particle Counter.

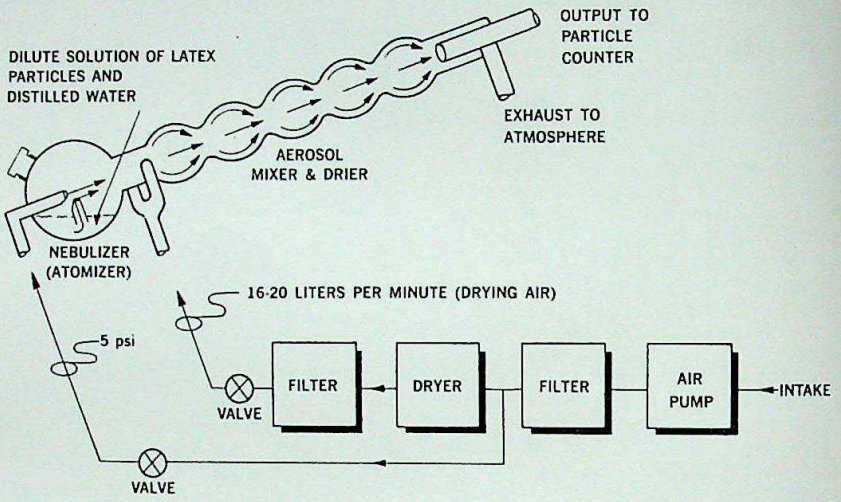


Figure 10. Design of the Royco Aerosol Generator, Model 255/6.

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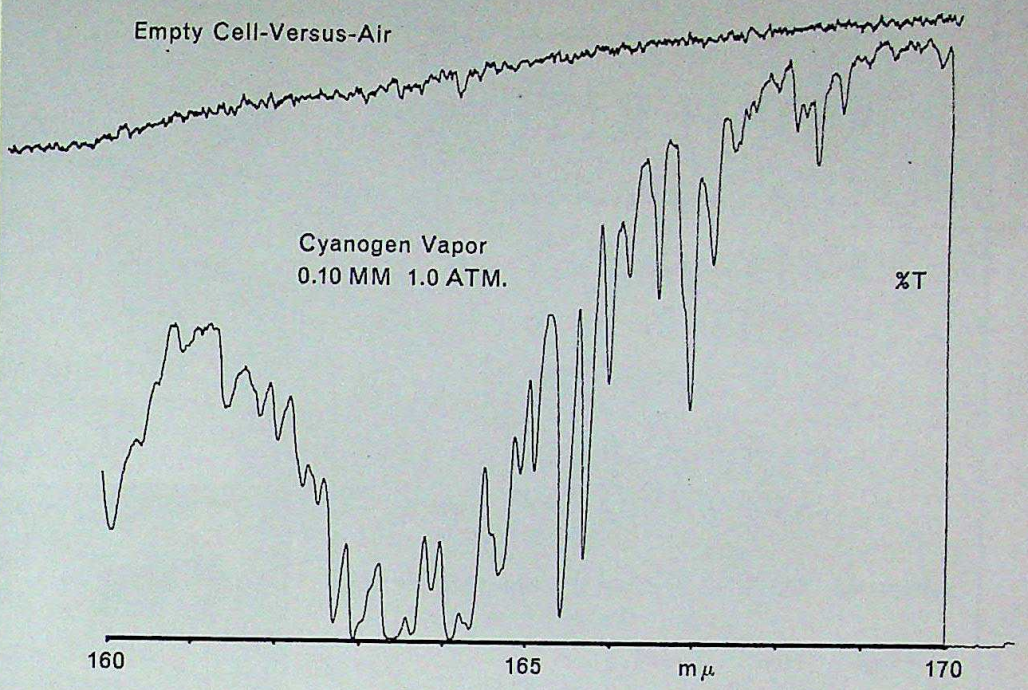
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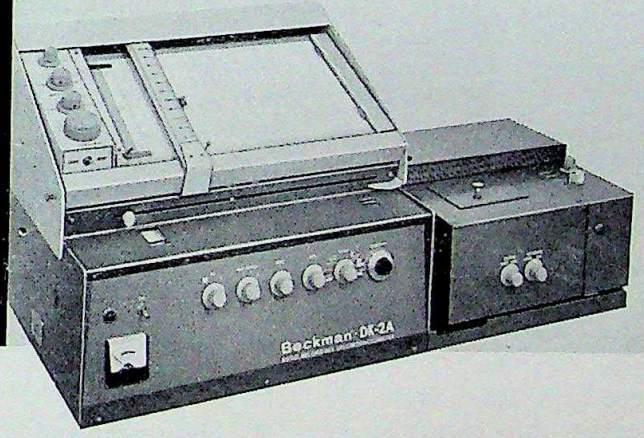
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now! go to 160 mμ without vacuum



New Beckman Far Ultraviolet DK-2A Spectrophotometer at work. Note the absence of hydrogen lamp line spectra and the high level of energy still available at 160-170 mμ. Both curves demonstrate negligible stray light.



From Beckman—first with a purged instrument to go to 185 mμ, then first to go to 170 mμ—comes another major advance in far-ultraviolet spectrophotometry. With the new Far UV DK-2A, you can perform analyses all the way to 160 mμ. It's a 15 mμ bonus over competitive instruments.

The Far UV DK-2A goes to the other extreme, too—3500 mμ. This is *the widest continuous wavelength range commercially available!* The Far UV DK-2A covers it with resolution of 0.2A for emission studies and 0.5A for absorption studies at 210 mμ. Consider also: 7 separate scanning speeds, multiple wavelength scale expansions, single-switch selection of 11 different chart ordinate presentations. Plus a wide variety of accessories.

Your Beckman Laboratory Dealer has the full Far UV DK-2A story. Also facts on the Far UV DK-1A if you want the same range in a strip-chart recording instrument. And for work in the 185-3500 mμ region, ask about the DK-1A with strip-chart recorder or DK-2A with flat-bed recorder. Contact him or write direct for Data File LUV-36-163.

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References

(1) Ind. Eng. Chem. 26–653 (June, 1933)

(2) Ind. Eng. Chem. 25–1112 (Oct., 1933)

(3) National Bureau of Standards Journal of Research 12-241 (Feb. 1934, R.P. No. 649)

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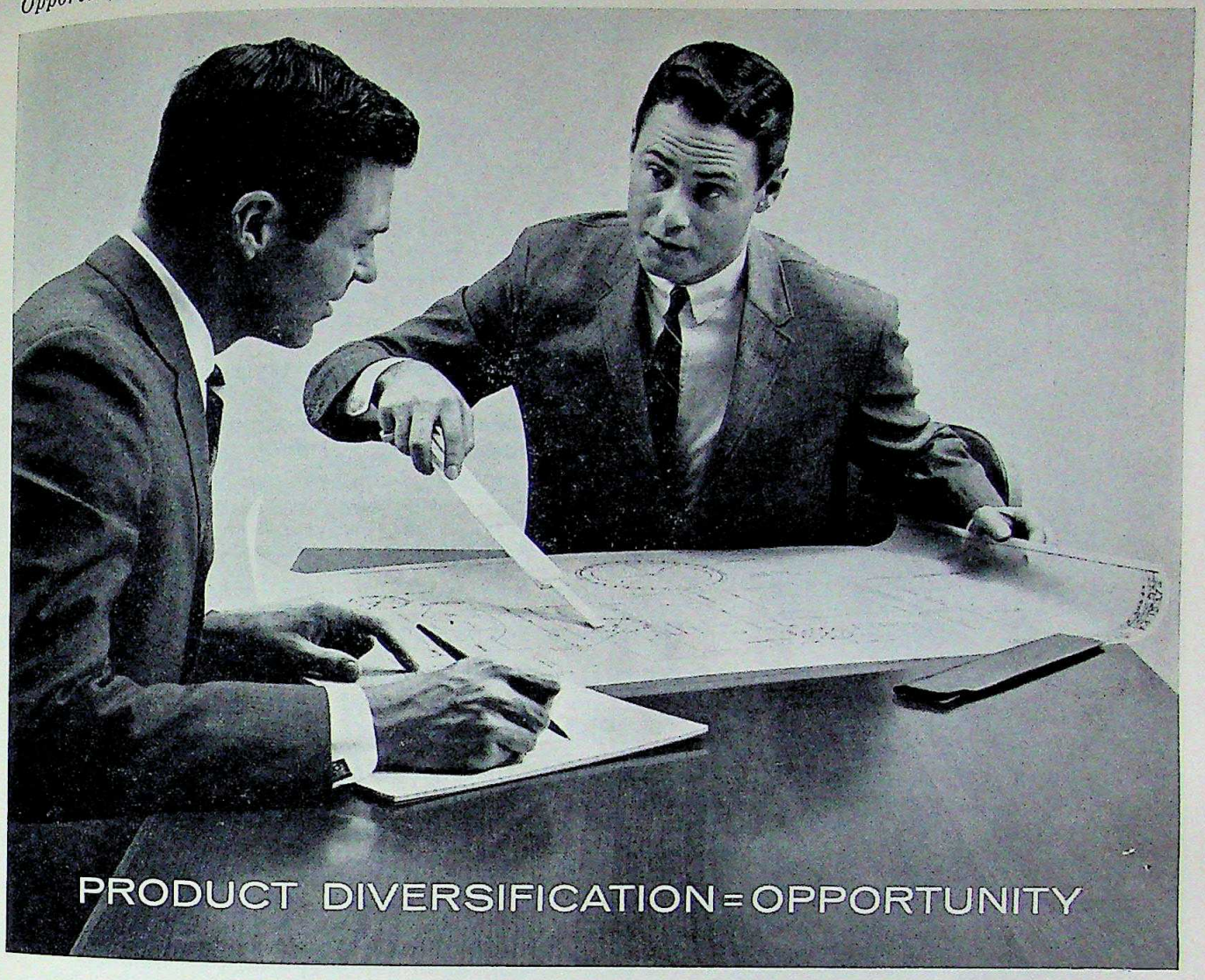
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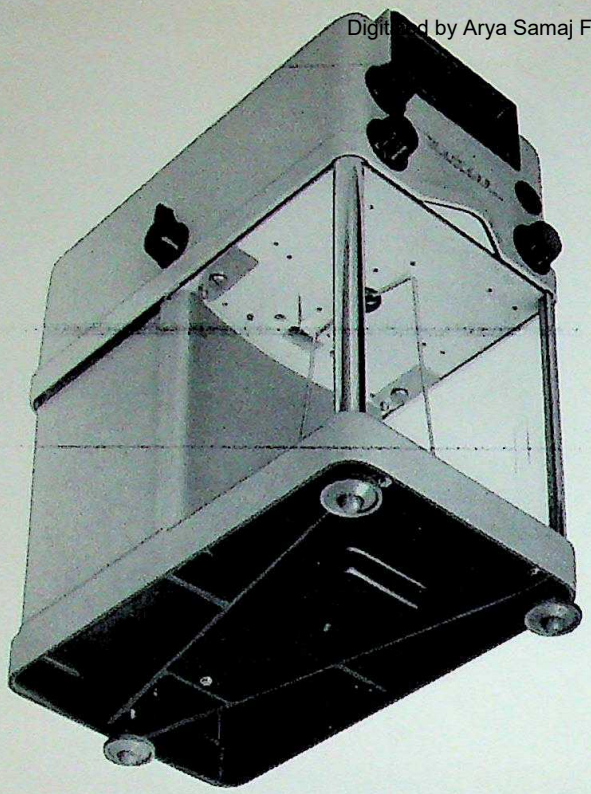
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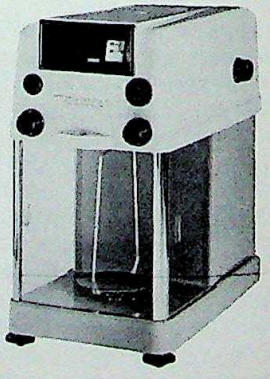
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Chem Ed

Out of the EDITOR'S BASKET

Edited by William G. Kessel

When writing for additional information about new products or for new literature, your inquiry will receive prompt attention if you write on your firm or Institution letterhead and mention the Journal of Chemical Education and the date of the particular issue. Pamphlets, booklets and similar literature are gratis unless otherwise specified.

New Apparatus and Equipment

▶ The Hot-Shot Boiler Division of Automatic Steam Products Corp. announces the availability of a new line of steam generators ideally suited for laboratory applications. The new units are completely glass lined to decrease the amount of contamination that would transfer in the steam, encountered in such applications as the use of steam as the carrier gas in gas chromatography. The Hot-Shot Jr. electric steam generator is available in five models and may be used for laboratory steam baths, autoclaving, and sterilizing, steam cleaning of small parts and many other laboratory uses involving steam. For further information write: Hot-Shot Division, Automatic Steam Products Corp., 3-7 West 61st St., New York 23, N. Y.

▶ A new, improved modular square wave polarographic analyzer, the Mark IV, for laboratory use has been introduced by Mervyn Instruments, Britain—a subsidiary of Gulton Industries, Inc., 212 Durham Ave., Metuchen, New Jersey.

▶ The "Titra-Kit," a package consisting of a Redox-pH Meter, a magnetic stirrer, an integrated support bar, stand and clamping device, and specially designed burettes, all of which can be used for simultaneous Redox and pH determinations as well as titrations is now available from Analytical Measurements, Inc., 490 Morris Ave., Summit, New Jersey.

▶ An improved version of Labindustries' all purpose repetitive reagent dispenser, capable of dispensing any reagent with 1% accuracy and 0.1% reproducibility, is now available from Labindustries, 1740 University Ave., Berkeley 3, California.

▶ Gaertner Scientific Corp., 1201 Wrightwood Ave., Chicago 14, Illinois, has announced production of an economically priced, small, divided-circle spectrometer, the L103, for the educational laboratory. A number of standard and new experiments are being developed for the L103 by Professor Edson R. Peck and will be available in booklet form from the company.

▶ Precise increments of current, as small as 10^{-13} amp, are available from the new Gyra current source, Model CS-57, for calibration of electrometers, or to buck-balance residual current from a detector. Contact Gyra Electronics Corp., P.O. Box 184, LaGrange, Illinois, for additional information.

▶ The Dannley pressure filter funnel, designed by Professor Ralph J. Dannley of Western Reserve University in cooperation with Ace Glass, Vineland, New Jersey, is particularly useful with volatile solvents and hot solutions which leave a residue on the underside of the disc when vacuum is employed.

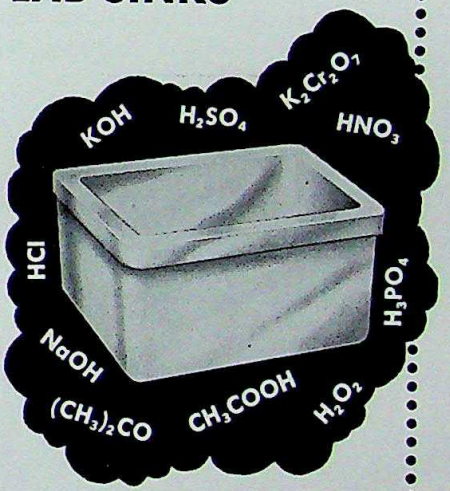
▶ Nucleonic Corp. of America, 196 DeGraw St., Brooklyn 31, New York, announces the development of a versatile, portable, battery operated electrometer, Model CP-1, that serves as a "cutie pie," a "one instrument" isotope laboratory and a calibrating instrument for microcurie to millicurie strengths of radioisotopes.

▶ Burrell Corp., 2223 Fifth Ave., Pittsburgh 19, Pennsylvania, recently introduced the Model KD Kromo-Tog, a high performance gas chromatograph with operating temperatures to 500°C, for the analysis of gases, liquids, and solids.

▶ Tennelec Instrument Co., P.O. Box 964, Oak Ridge, Tennessee, offers the

(*Continued on page A281*)

"U.S." CHEMICAL PORCELAIN LAB SINKS



. . . handle ALL corrosives safely

No more need for corrosion charts . . . for special sinks for special corrosives, with the chances of costly mistakes.

Time-proven "U. S." Chemical Porcelain laboratory sinks will handle safely all acids, alkalies, caustics and solvents — weak or strong, hot or cold. With normal routine rinsing, even hydrofluoric acid presents no problem. "U. S." Chemical Porcelain laboratory sinks will also withstand all the heat shock and physical abuse they'll ever meet in normal laboratory use.

Available in three attractive colors — cool "surf green," soft "mist gray" and sparkling white — these strong, non-staining, scratch-resistant sinks are as easy to clean as a china dish. Over one hundred different styles and sizes are available to meet every need.

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New Torsion 1,000 gram balance speeds laboratory work

Only Torbal 1/10 gram PL-1 offers all these features

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Price only $525.

To give you more convenient, accurate readings, Torsion has designed the PL-1 with a fine-reading vernier to 1/10 gram and a capacity of 1 kilogram. The balance has an optical range of −10 grams to +110 grams.

The heart of the mechanism in the new PL-1 is the Torsion no-knife edge construction. This eliminates friction and wear, insures lifetime accuracy and speeds weighing. The balance will operate accurately even in severely corrosive or dust-laden atmospheres.

Taring through a 125 gram range is accomplished with a built-in knob on the side of the balance. By using the second pan the balance can be made to tare up to 325 grams. Torsion's optical projection Model PL-1 offers a sharp image with a high degree of illumination for easy reading and an oil damper to speed up weighing.

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THE TORSION BALANCE COMPANY

TORBAL

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Out of the EDITOR'S BASKET

Model TC 150, a universal preamplifier of exceptional versatility designed by E. Fairstein for difficult nuclear measurements. It provides excellent resolution and high count-rate capabilities with semiconductor detectors, low-energy beta proportional counters, and pulse ion chambers. A complementary model, the TC 150 FC, is for use with reactor fission chambers.

▸ A new high quality, high resolution, thermal conductivity analytical gas chromatograph, the Anakro IA, has been announced by Nester/Faust Mfg. Corp., 2401 Ogletown Rd., Newark, Delaware.

▸ Waters Associates, Inc., 45 Franklin St., Framingham, Massachusetts, have developed a new miniature liquid analyzer, the Milan, for either continuous or batch monitoring of various liquid state components in applications. The principle of operation of the Milan is the measurement of the amount of reflected light from the interface of a flowing liquid stream and the surface of a hollow glass tube which serves as the flow path through the analyzer.

▸ Con-O-Saw fills a widespread need for a basic tool capable of cutting difficult materials. It was developed for Continental Sensing Inc., 1960 Ruby St., Melrose Park, Illinois, to cut precious metals and ceramics with little waste, no burrs and no distortion. Its unique capability should make it useful in electronic and chemical laboratories, for any work involving precise cutting of intractable materials.

▸ From General Scientific Equipment Co. comes a new face shield to protect eyes, face and under chin where splashing is a problem. Worn with a safety helmet, full, wide, unrestricted vision and audibility is provided by the new shield, named, "The Mark I." Complete information may be obtained by requesting *Bulletin #17* from the General Scientific Equipment Co., Limekiln Pike and Williams Ave., Philadelphia 50, Pennsylvania.

▸ McPherson Instrument Corp., 530 Main St., Acton, Massachusetts, offers Model 630 high energy vacuum U.V. Hinteregger type discharge lamp with a direct and positive cooling method as a unique feature.

▸ Joseph Kaye & Co., Inc., 737 Concord Ave., Cambridge, Massachusetts, has recently introduced a new line of dc variable-output power supples to be used primarily for powering thermoelectric devices in general laboratory research.

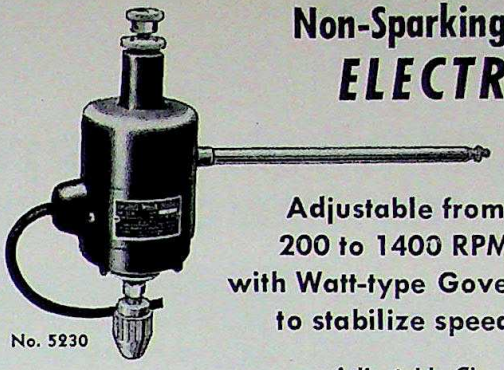
▸ For information on short term rental or long term lease of ultra-high speed photo-instruments write Jack Patterson, Field

(*Continued on page A282*)

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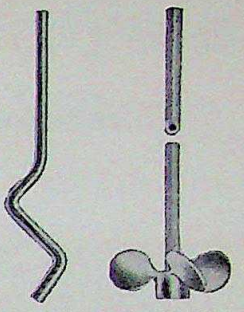
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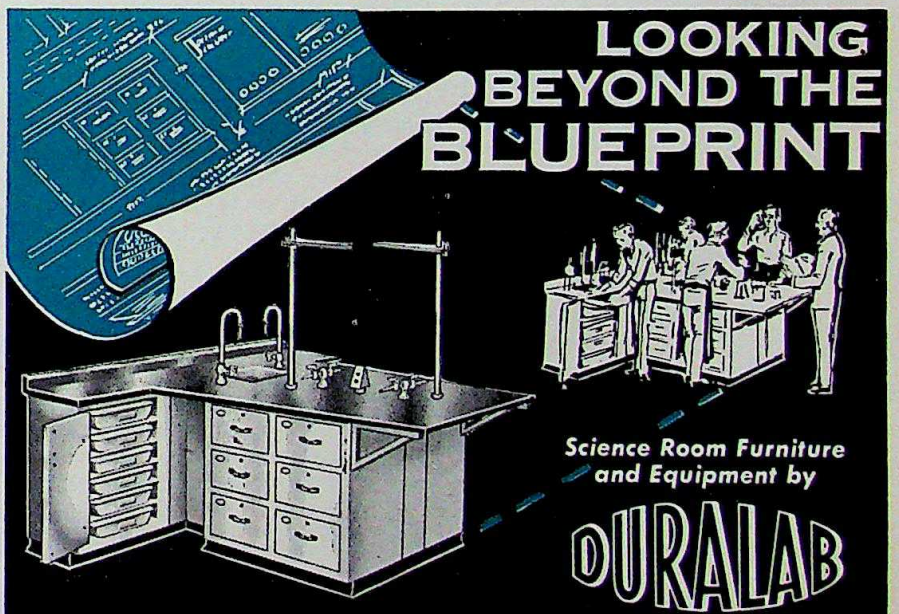
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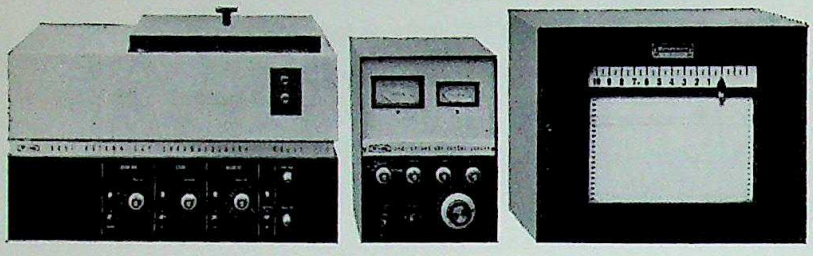
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model 700 gas chromatograph



Model 700 Features

Dual columns
Hot-wire thermal conductivity detector
Separate temperature control on column, detector and injection port to 400°C
Large capacity, low mass oven accommodates up to 150 ft. of ¼ in. OD column
Manual temperature programming
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Integral DC power supply
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Preparative columns and accessories
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The Model 700 is an important adjunct to F & M's line of research gas chromatographs. It is ideally suited for separations which must be frequently repeated. The design and rapid heating and cooling characteristics of the column oven makes it possible to quickly and easily interchange columns without baseline disruption. It is also useful as a teaching instrument incorporating such gas chromatographic features as dual column operation, high temperature performance and temperature programming.

The F & M Model 701 is the same as the 700 except that it includes proportional temperature control on the column oven and a DC bridge power supply.

For more information on the Model 700, other F & M instruments and a copy of the new F & M Columns and Accessories Catalog, write to F & M Scientific Corporation, Route 41 and Starr Road, Avondale, Pennsylvania, 215-COlony 8-2281. *European Subsidiary: F & M Scientific Europa N. V., Leidestraat 67, Amsterdam, The Netherlands.*

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Out of the EDITOR'S BASKET

Sales and Service Manager, Beckman and Whitley, Inc., San Carlos, California.

▶ In response to demand of chemists and laboratory personnel for a balance of 1000 gm. capacity and 0.1 gm. accuracy, The Torsion Balance Co. of Clifton, New Jersey, is introducing its new Torbal PL-1 optical projection balance.

▶ Wilkens Instrument and Research, P.O. Box 313, Walnut Creek, California, announce a new gas chromatograph specifically designed for pesticide residue analysis. Named the "Aerograph Pestilyzer," the instrument utilizes the unique concentric tube electron capture detector.

▶ Pfaltz and Bauer, Inc., Empire State Bldg., New York, N. Y., offer the new Bunge "25 UM" Ultra-Micro balance. It has a 2 mg. optical scale, 9 mg. automatic weight loader and 2.5 g. built-in tare weights for a total capacity of 2.511 g., with a sensitivity of 0.1 μg, with estimations to ± 0.01 μg.

▶ Needs Corp., 255 W. Euclid Ave., Jackson, Michigan, announces a new line of unbreakable graduated cylinders and hydrometer jars made of a new glass-transparent polycarbonate plastic.

▶ The Gow-Mac Instrument Company announces a new kit for an experimental chromatograph, which is easily assembled with standard tools, and can be used with a 12 volt storage battery and any 0–10 millivolt fast-pen strip chart potentiometer recorder. The GC Gas Kit includes all parts necessary for electrical circuitry and flow system.

Assembly of the chromatograph and instruction in analysis of gases and volatile liquids are described in "Experimental Gas Chromatography" by Dr. J. M. Miller of Drew University. This laboratory manual details twelve student-tested experiments directed to organic, inorganic and physical chemistry applications at college and technical school level. The GC Gas Kit includes the Gow-Mac 9285 pretzel detector with four tungsten filaments, new Gow-Mac heated injection block, materials for construction and packing of chromatographic columns as well as the text and instructor's manual.

Complete information and price available from Gow-Mac Instrument Co., 100 Kings Rd., Madison, New Jersey.

▶ The DK06 Multi-Decameter for precise determination of the dielectric constant and the dielectric loss by highly sensitive oscilloscope and meter indicators respectively is now available from Kahl Scientific Instrument Corp., P.O. Box 1166, El Cajon (San Diego) California. With an accuracy up to 0.01%, this variable frequency generator covers the range from 100 kilocycles to 12 megacycles. Water jacketed sample measuring cells are avail-

(*Continued on page A284*)

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Coleman instrumentation for automated combustion analysis

Complete determinations in only 8 minutes
. . . improve accuracy and reproducibility
. . . eliminate errors due to variations in analytical technique.

For nitrogen analysis—the time proven Coleman Nitrogen Analyzer is unequalled in speed, reproducibility and convenience by any traditional method for total nitrogen determination. It provides rapid and automatic performance of all steps required in the analysis.

WIDE APPLICATION—the instrument is ideal for virtually any solid or liquid material that dissociates at temperatures up to 1100° C.—including materials usually analyzed by time-consuming Kjeldahl procedures.

DIRECT READING—results of the analysis are displayed on a digital counter.

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Write for descriptive literature and reprint of complete evaluation report by Southern Research Institute.



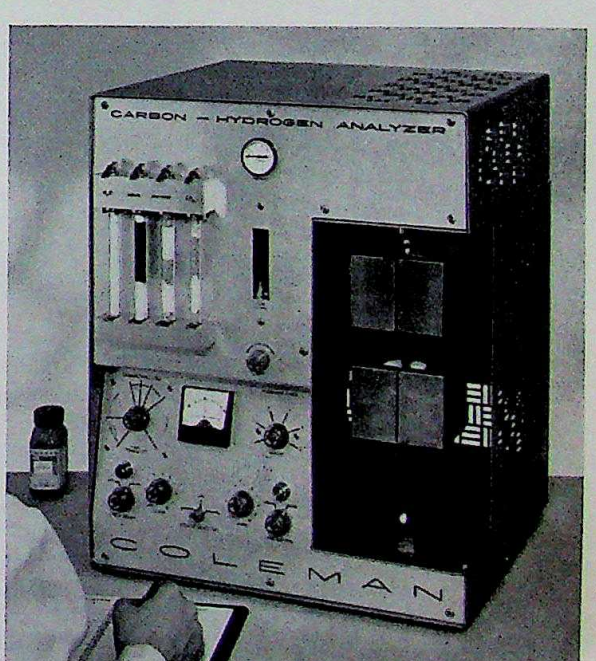
For carbon and hydrogen analysis—the Coleman Carbon-Hydrogen Analyzer, an automated combustion train, offers substantial advantages over conventional methods. Greater speed, convenience and improvements in precision and accuracy result from the instrument's performing all operations in exactly the same manner. Benefits include:

VERSATILITY—Variables of the combustion cycle are readily programmed to meet requirements of a wide variety of sample materials—hydrocarbons as well as materials containing oxygen, nitrogen, sulfur and halogens. Specially-prepared silver vanadate and manganese dioxide reagents, available from Coleman, permit analysis of difficult samples.

RANGE—the instrument is valuable in laboratories concerned with feeds, pharmaceuticals, petroleum, organic intermediates, heavy chemicals and biological materials. It is used for analysis of materials containing 10-98% carbon and 0.5-15% hydrogen.

ACCURACY—automatic control of the major variables in the analysis—temperatures, flow rates, combustion periods—provides high analytical accuracy. For routine work, the instrument results correspond to theory ±0.2% carbon and ±0.2% hydrogen.

Ask for Bulletin BB-275.



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able for all media including powder immersion technique. Simple and quick to operate, the DK06 Multi-Decameter is suitable for laboratory research, quality or industrial control (binary or tertiary systems; trace water determination; aging or oxidation; distillations; etc.) applications.

New Literature

● Four topics discussed in the Englehard Industries *Technical Bulletin* (Vol. III, No. 3) released recently include: "Gold Plating by Immersion," "Stereochemistry of Hydrogenation of Xylenes with Rhodium and Ruthenium Catalysts," "The Growth History of Diamonds as Revealed in Etched Cross Sections," and "Inorganic Films for Solar Energy Absorption." Copies of the *Technical Bulletin* may be obtained from the Technical Service Dept., Engelhard Industries, Inc., 75 Austin St., Newark 14, New Jersey.

● A brochure titled *Chemicals For Industry* has been published by the Plastics Div., Allied Chemical Corp., 40 Rector St., New York 6, N. Y. More than 100 basic chemicals are described and major applications suggested in the 24 page booklet.

● How to apply statistics to nuclear measurements is the subject of Nuclear-Chicago's latest *Technical Bulletin No. 14*. This bulletin describes the variations which are encountered by the experimenter when making radioactivity measurements. It explains why these variations occur, how they can be predicted, and how to determine statistical accuracy. Write Nuclear-Chicago Corp., 359 E. Howard Ave., Des Plaines, Illinois.

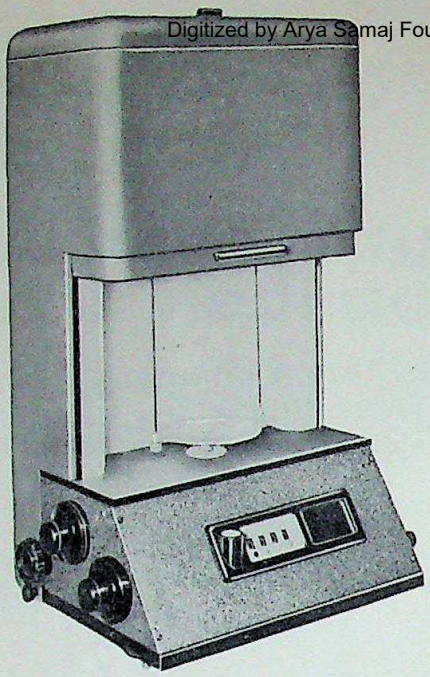
● *Price List E* gives information on Deuterium Oxide (regular and low concentrations), Deuterium Gas, Deuterium enriched compounds, Nitrogen^{15} enriched compounds, Carbon^{13} enriched compounds, Oxygen^{18} enriched compounds and Oxygen^{17} enriched compounds. Copies may be obtained by writing Bio-Rad Laboratories, 32nd and Griffin Ave., Richmond, California.

● The Sargent *Bulletin ST-1* describes in detail the Sargent spectrophotometric and potentiometric automatic titrators and their applications. Write for a copy to Dept. ST, E. H. Sargent & Co., 4647 W. Foster Ave., Chicago 30, Illinois.

● A 24-page catalogue covering: electromagnets, highly stabilized power supplies, nuclear magnetic resonance gaussmeters and control systems, accessories; for numerous activities including EPR, NMR, materials research, solid state studies, Zeeman and Faraday effects, beam handling, MHD, and others is availabe on request from Harvey Wells Corp., Framingham, Massachusetts.

● Standard Scientific Supply Corp., 808

(Continued on page A286)



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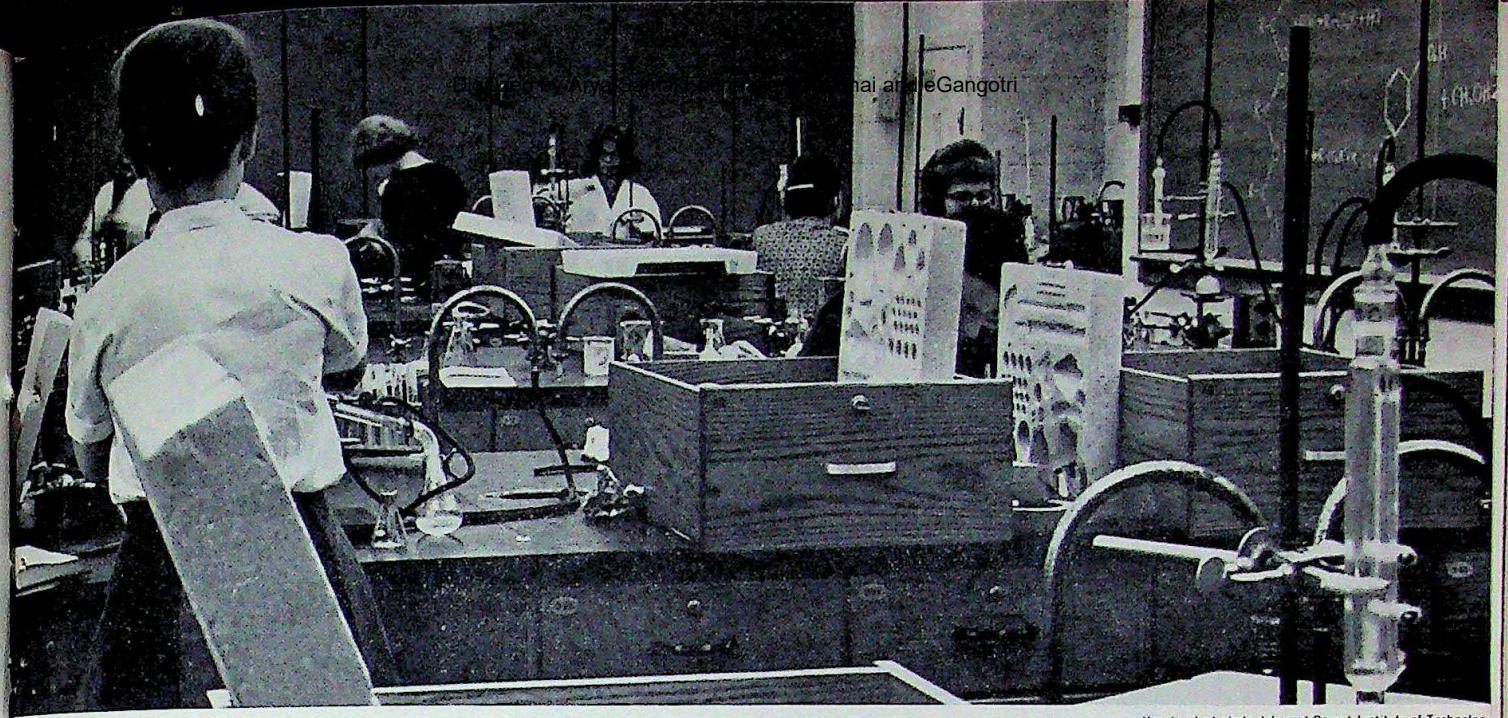
Models CL1 and CL2 have a capacity of 200 grams; sensitivity per Vernier division is 0.1 milligram for the CL1 and 1.0 milligram for the CL2. Price is a modest $750 each. Model CL3 has a capacity of 100 grams with a sensitivity of 0.01 milligram per Vernier division. Price is $1,050.

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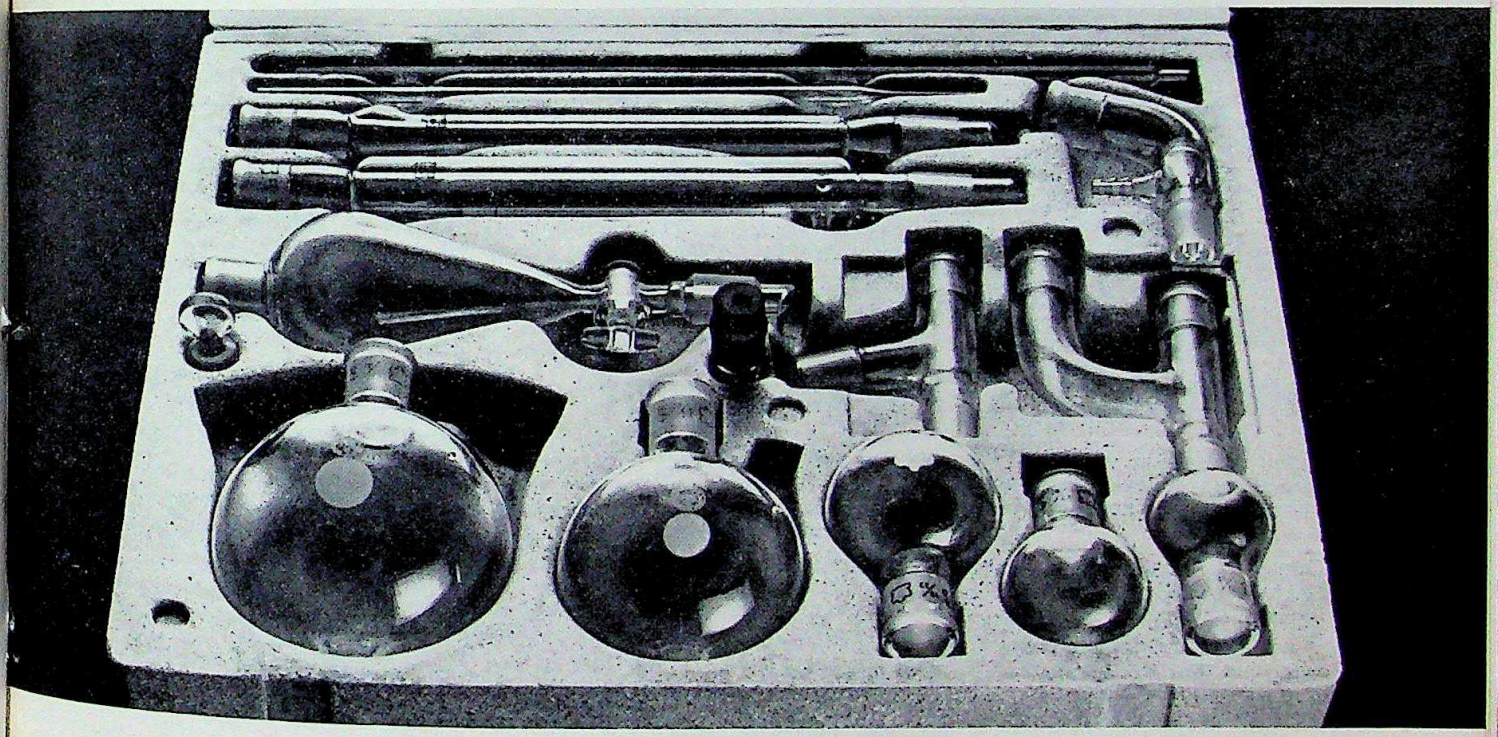
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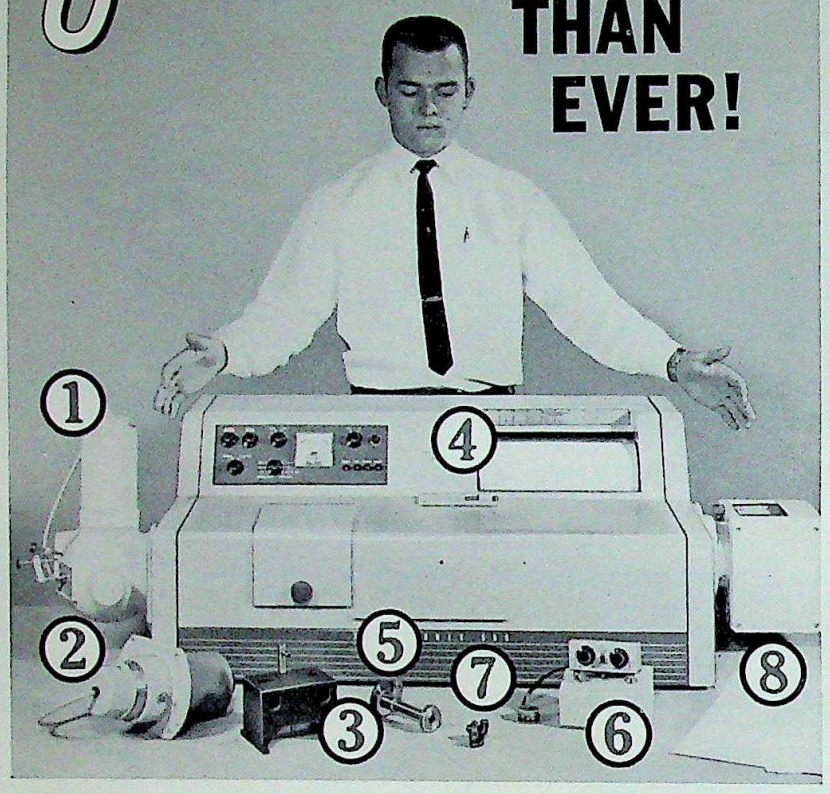
There's much more you should know about Kontes Kem-Kits: The several kit types available. How only fifteen parts enable such a variety of set-ups. Why ultimate cost is less than cork equipped labs. For complete information send for Bulletin 962-R.

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Rest of the EDITOR'S BASKET

Broadway, New York 3, N. Y., announces publication of a new series of quarterly bulletins, titled *Lab Apparatus*, a review of current developments in laboratory equipment and apparatus. Available on request.

● A new 12-page brochure titled *Norelco Cryogenerators for Low Temperature Applications* is available from Cryogenerators, Division of North American Philips Co., Inc., Mendon and Angell Rds., Ashton, Rhode Island.

● Capabilities of CEC's new first order angular focusing mass spectrometer with a 60° sector magnetic field on a 12-in. radius are described in an 8-page *Bulletin 21703* from Consolidated Electrodynamics Corporation, 360 Sierra Madre Villa, Pasadena, California.

● Mettler Instrument Corp., 20 Nassau St., Princeton, New Jersey, is offering literature on their new M5 and M5 S/A micro balances. These instruments are designed for rapid and convenient handling of small samples for chemical analysis, assay work, and for weight control of very fine parts.

● Rectilinear graphic recording instruments which use no elaborate pulleys and fish-wires to translate curvilinear into rectilinear motion are described in a four-page two color Esterline Angus catalogue. Request a copy from Esterline Angus Instrument Co., Inc., P.O. Box 596, Indianapolis 6, Indiana.

● A new 52-page catalogue *D*, describing a broad range of nuclear accessories and related instruments for radioisotope users in research, industry, medicine and education, is available from Atomic Accessories, Inc., 811 W. Merrick Rd., Valley Stream, New York.

● Volk Radiochemical Co., 8260 Elmwood Ave., Skokie, Illinois, announces its revised and expanded *Labeled Compounds for Research Catalogue* of available compounds to meet the ever-increasing needs of biological, chemical, and medical research.

● A 6-page illustrated folder giving details, prices and applications of *Standardettes*, Chemical Standards, is available from Chemical Service Laboratories, P.O. Box 464, Largo, Florida.

● New catalogue includes several labeled compounds not hitherto available and appreciable price reductions on several others. *Catalogue No. 5122.* Isotopes Specialties Co., Box 688, Burbank, California.

● A new *Bulletin MFS-1* describing a multi-channel flame spectrometer that analyzes magnesium, calcium, sodium, potassium and other metals simultaneously

(*Continued on page A293*)

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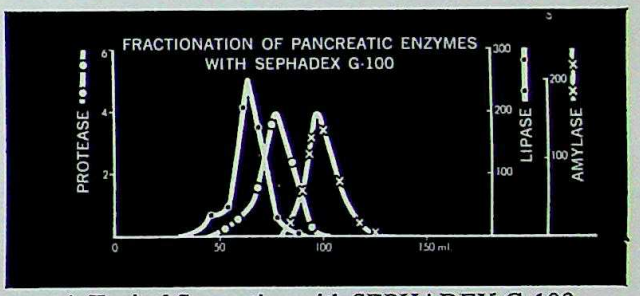
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A Typical Separation with SEPHADEX G-100

Sample: 3 ml. of an extract of powdered swine pancreas in 0.05 M acetate buffer pH 5.3 containing 0.005 M calcium acetate.
Column size: 117 ml. (2 x 37 cm.).
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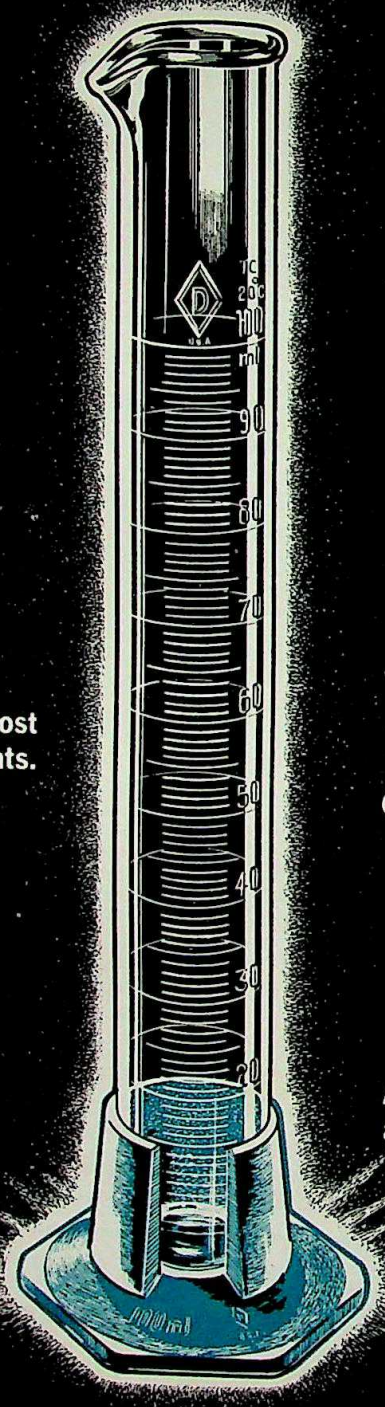
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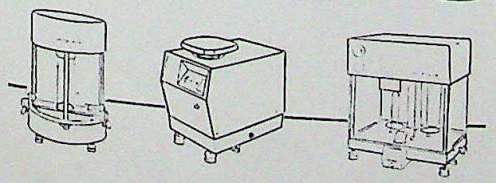
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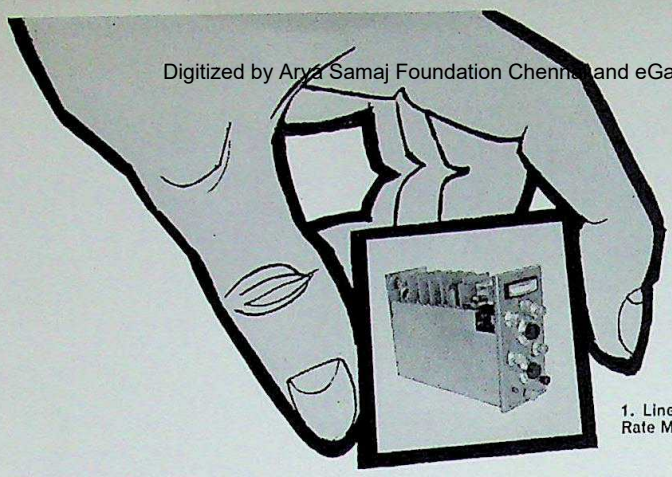
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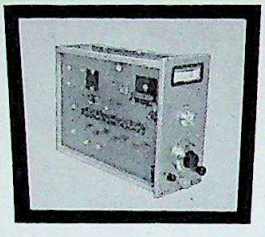
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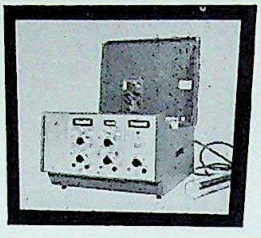
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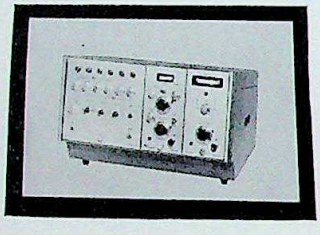
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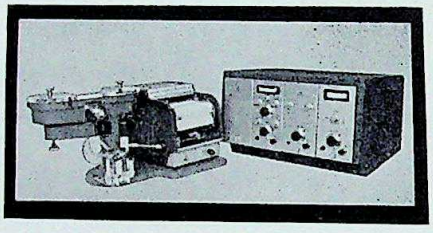
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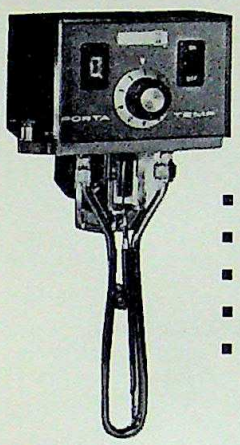
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Out of the EDITOR'S BASKET

has been announced by Technicon Instruments Corp., Research Park, Chauncey, New York.

● A new 36-page catalogue, entitled *KSE Enclosures* describing glove, vacuum and dry boxes has just been released by Kewaunee Scientific Equipment, 4080 Logas St., Adrian, Michigan.

● For information on the Dri-Cool liquid carbon dioxide freeze dryer write to Robert Goldsmith, Associated Testing Laboratories, Inc., 200 U. S. Highway 46, Wayne, New Jersey.

● *Specialty Chemicals for Research* is the title of *Catalogue D-267* available from the Borden Chemical Co., Dajac Laboratories, 5000 Langdon St., Philadelphia 24, Pennsylvania.

● The complete line of Parr combustion bombs and calorimeters is shown in a new 20-page illustrated price list, *Parr No. 63-1*. The complete line of Parr pressure reaction apparatus is shown in a new 20-page illustrated price list, *Parr No. 63-2*. Copies of the above will be mailed on request. Write Parr Instrument Co., Inc., 211 53rd St., Moline, Illinois.

● *Bulletin No. 3001e* giving information on chemical stability of SK, SSK, and BaF glasses produced by Janaer Glaswerk is available from Fish-Schurman Corp., 70 Portman Rd., New Rochelle, N. Y.

● Recent work in countercurrent fractionation is compiled in a 45-page bibliography by E-C Apparatus Corp., 538 Walnut Lane, Swarthmore, Pennsylvania.

● Tracerlab, 1601 Trapelo Rd., Waltham 54, Massachusetts, now offers a new illustrated 80-page *General Catalogue*, containing information on the most complete line of nuclear instruments and services available. Also available is a new *Radiochemical Price List*.

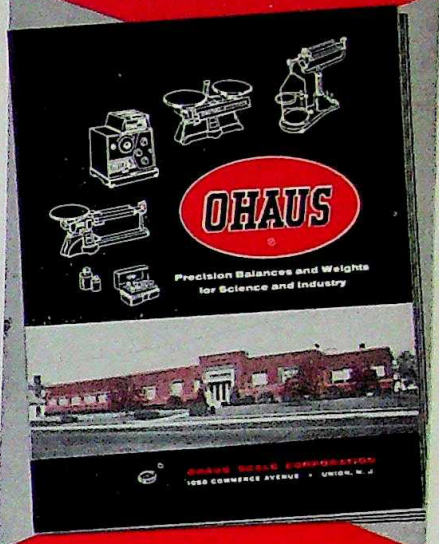
● Information on the now available, *Electrical and Chemical, National Catalogue of Patents* may be obtained from Rowman and Littlefield, Inc., Publishers, 84 Fifth Ave., New York 11, N. Y.

● F & M Scientific Corp. of Avondale, Pennsylvania has made available the 12-page current edition (Vol. 3, No. 2) of their house organ *Facts & Methods For Scientific Research*. This edition includes a feature article, "The Science of Programmed Temperature Gas Chromatography," by Dr. J. C. Giddings, Department of Chemistry, University of Utah.

● An eight-page two color brochure contains technical description, schematic specifications and application of a wide range model HLVC-150 Log-voltmeter-converter. Write Houston Instrument Corp., 4950 Terminal Ave., Bellaire 101, Texas.

(*Continued on page A294*)

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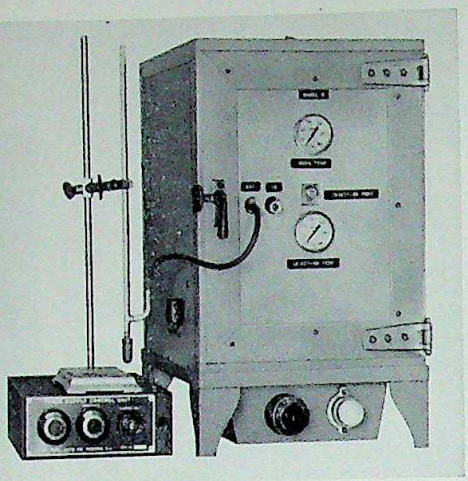
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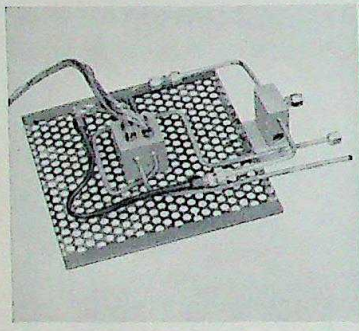
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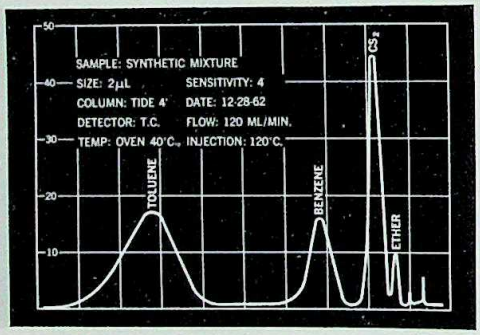
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● For a copy of *Photomultiplier Tube Catalogue T-1* describing over 35 tubes, write Electron Tube Div., EMI/US, 1750 N. Vine St., Los Angeles 28, California.

● *Technical Bulletin No. 104* describes five newly available compounds produced by Gallard-Schlesinger Chemical Mfg. Corp., 1001 Franklin Ave., Garden City, L.I., New York.

● The following is available from the O.T.S. U. S. Dept. of Commerce, Washington 25, D. C. AD 278 353. The publication is *Basic Studies on Fuel Cell Systems.* G. B. Adams and others, Lockheed Missiles & Space Co., for the U. S. Navy, May, 1962. 79 pages. $2.00.

New Chemicals

◇ A new series of silica gel powders for thin-layer chromatography are now available from Applied Science Laboratories, Inc., State College, Pennsylvania.

◇ Volk Laboratories, 8260 Elmwood Ave., Skokie, Illinois, provide a radio-iodination service for researchers who wish to undertake radioiodination of any compound whose chemistry appears suitable.

◇ Simplified standard irradiation service is now available from U. S. Nuclear Corp. It is a minimal cost service for samples which will fit into standard containers for doses from 100 to 107 roentgens. Custom instrumented or special environment service also available. U. S. Nuclear Corp., P.O. Box 208, Burbank, California.

Miscellany

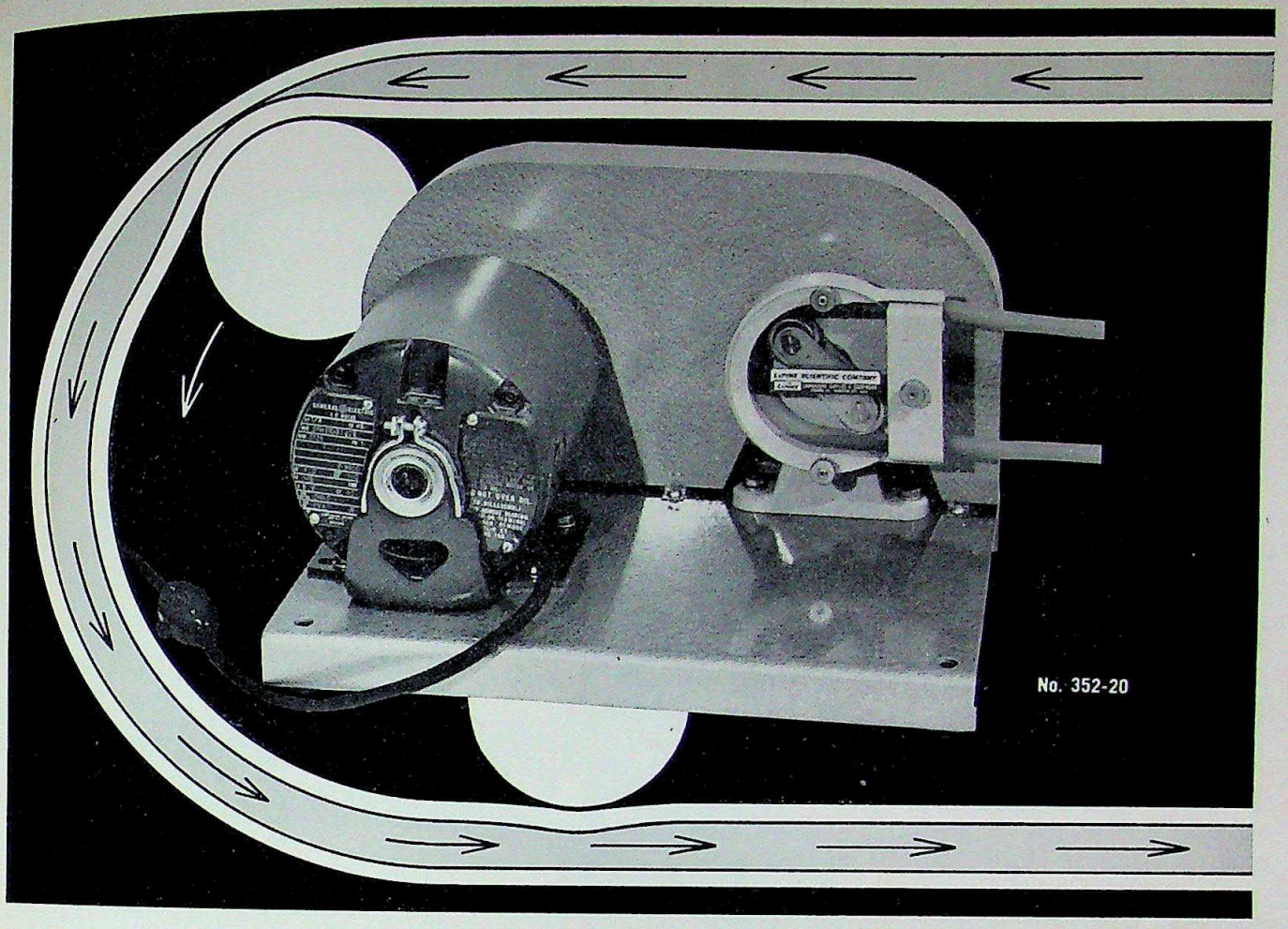
★ The Invitation to the European Convention of Chemical Engineering and the Achema Congress 1964, the 14th Chemical Engineering Exhibition - Congress, in Frankfurt am Main, 19th–27th June 1964, has been published. Readers can obtain the 40-page brochure, format DIN A 4 (210 × 297 mm), on request from the Dechema Deutsche Gesellschaft für chemisches Apparatewesen E. V., 6 Frankfurt (Main) 7, Postfach 7746.

★ A new electronic test scoring machine that promises to be a boon for busy teachers and a unique learning experience for students is being introduced on the educational market. Information on the "Grademaster" is available from Electronics for Education, Inc., 10582 Metropolitan Ave., Kensington, Maryland.

★ Information on graduate study in "Communication Theory and Technical Writing" leading to the Master of Science degree at Rensselaer Polytechnic Institute, may be obtained from Dr. Sterling P. Olmsted, Department of Language and Literature, Troy, New York.

(*Continued on page A298*)

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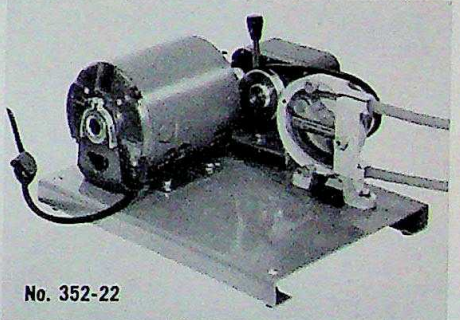
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★ Keeping in step with President Kennedy's Advancement of Scientific Studies Program, Kontes Glass Co. of Vineland, New Jersey has instituted a Merit Award Program for Outstanding Achievements in the Field of Scientific Instruction. First recipient of this award is Mr. J. Albert Starkey, Chairman of the Science Department of Vineland High School. Mr. Starkey was selected for this award by the South Jersey Section of the American Chemical Society. The Vineland High School received ten Kontes laboratory glassware "Kem-Kits" awarded in Mr. Starkey's name at the first assembly held in this new four million dollar school.

★ Adaptable Laboratory Furniture Co., Inc., 145 Nassau St., New York, N. Y. announces a new service which should fill a long-felt need in industrial, government and educational laboratories. The company, which designs and manufactures the Adapt-A-Lab line of modular laboratory furniture and equipment, is now offering a specialized consultant service geared to the design requirements of specific individual laboratory installations.

★ Dr. Wouter Bosch, Missouri School of Mines and Metallurgy, Rollo, Missouri announces two new summer courses, Polymer Orientation and Conference on the Chemistry and Physics of Polymers. Information will be furnished on request.

★ General Electric Co. recently announced the establishment of Advanced Technology Laboratories in Schenectady for development work leading to broad new opportunities for American business and industry. The new laboratories—chemical and materials, electrical, information and mechanical—succeed the Company's 67-year-old General Engineering Laboratory, one of the oldest industrial engineering laboratories in the country.

★ The Canisius College Department of Chemistry announces its second annual Nuclear Magnetic Resonance Spectroscopy Institute to be held at the College from June 24–28. Simultaneous elementary and advanced sessions will be held. The elementary sessions are for those beginning NMR Spectroscopy and will emphasize basic theory and extensive interpretation of spectra. The advanced sessions will be designed for those having a background in mathematics who wish to become acquainted with the fundamental theory of magnetic resonance, spin decoupling techniques and conformational analysis. For further information contact Dr. Herman Szymanski, Chairman, Dept. of Chemistry, Canisius College, 2001 Main St., Buffalo 8, New York.

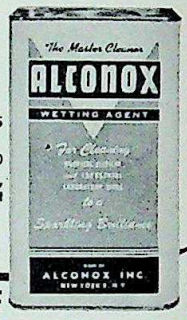
★ A 32-page reprint of the articles by Hubert N. Alyea in his "TOPS in Chemistry" series which ran in the *Science Teacher* in 1962, is now available. Single copies of this reprint may be purchased at $1.50 each from the National Science Teachers Association, 1201 16th St., N.W., Washington 6, D. C.

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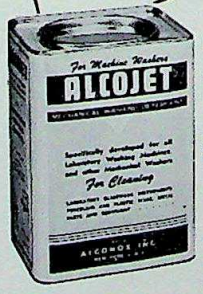
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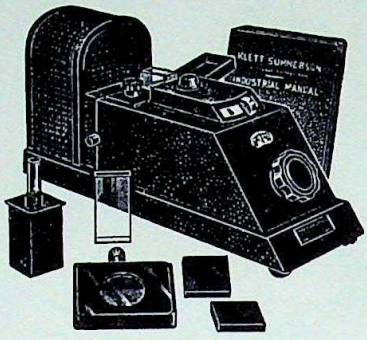
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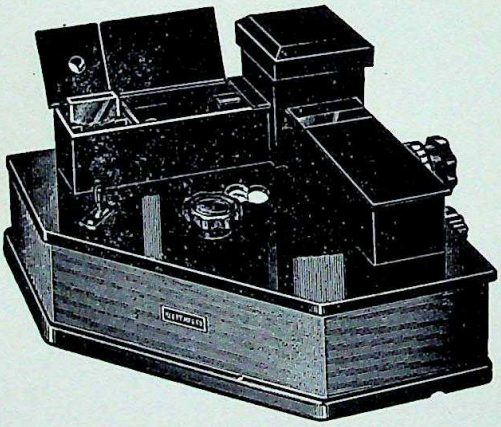
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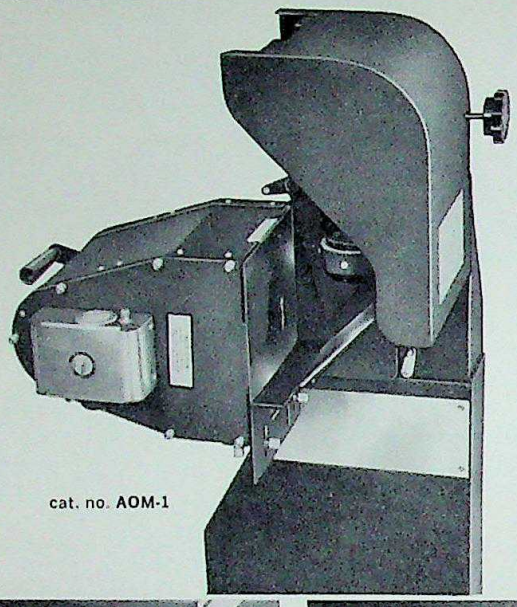
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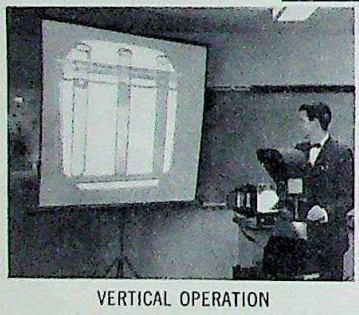
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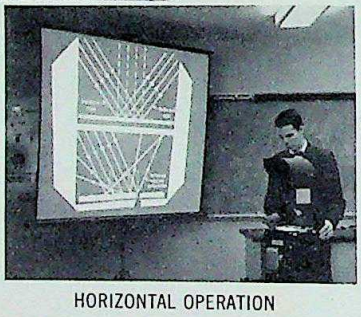
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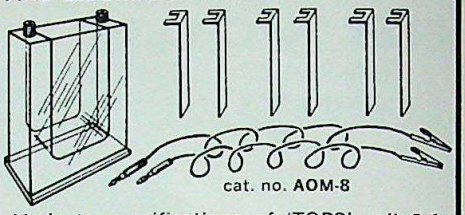
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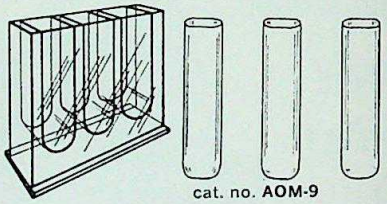
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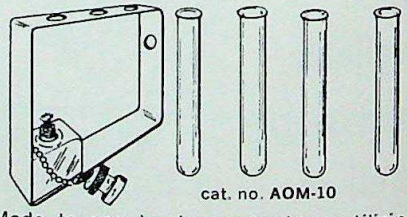
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3. HYDROGEN

A. Historical

Hydrogen an Element

See Dem. 65, hydrogen from Zn + acid. Recall Dem. 9, oxygen from HgO. Cavendish used these preparation methods, then combined $2H_2 + O_2$ to show water is a compound, not an element.

Dem. 65—Zinc + Acid

To show: The preparation of hydrogen by the action of an acid upon a metal, the method used by Cavendish in 1881 when he discovered hydrogen. $Zn + 2HCl \rightarrow ZnCl_2 + H_2$; $2H_2 + O_2 \rightarrow 2H_2O$.

Materials: Cell G-1 with gas holder, mossy or granular Zn, dil. HCl.

Procedure: Fill reaction chamber of G-1 one-fifth full of the Zn. Fill the dropper with dil. HCl. Add water to the shoulder of the other chambers. Project. Drop acid on the Zn. Lower the gas holder, then stopper. When holder is full of hydrogen, remove and ignite.

Observation: Hydrogen is evolved, and explodes to form water which condenses inside of the gas holder.

Note: The first holderful of gas may be mostly air. Repeat the collection until the off-gas explodes.

Dem. 66—H-O Formation and Re-combination

See Special Devices SD-11. In it dil. H_2SO_4 is electrolyzed to give 2:1 volumes of H:O; then this mixture is exploded to give H_2O.

B. Preparation of Hydrogen

1. FROM METAL + COLD WATER

Dem. 67—Na and K on Water

To show: A comparison of the reactivity of sodium and potassium on water. $2Na + 2HOH \rightarrow 2\,NaOH + H_2$; $2K + 2HOH \rightarrow 2KOH + H_2$.

Materials: Plastic box $4\frac{1}{2} \times 4\frac{1}{2} \times 1$ in., Na, K, marking pencil, Tide detergent, tongue depressor (wooden paddle).

Procedure: The same as for Dem. 2, excepting that the tongue depressor is placed diagonally in the box to form two triangular boxes, one marked Na and the other K. Add water and Tide but not the indicator. At the same instant drop equal size bits of Na and K into their boxes. Cover boxes at once to protect lens.

Observation: The potassium fizzes and clouds up its box almost at once; the sodium in its box reacts vigorously, but not instantly.

Note: *1.* Either the horizontal projector stage, or the vertical stage with Horizontalizer Ho can be used.

2. It is also instructive to include lithium in this demonstration. Although lithium is above sodium in the E.M.F. series, measured of course in an entirely different manner, it does not react so vigorously. E.M.F. values: Li 3.05, K 2.99, and Na 2.71.

Dem. 68—Li, Ca, and Na-Pb Alloy on Water

To show: Relative activities of some metals with water.

Materials: Cell C-g2(SD-7), lithium, calcium shavings, sodium-lead alloy obtainable from J. T. Baker Co., Phillipsburg, N. J.; phenolphthalein indicator solution.

Procedure: (*a*) Place small bits of the metals in culture tubes. A pin-head of the Na-Pb alloy is best, or it will churn black during reaction. Now run one-half a tube of water upon each. Project. (*b*) After a minute test the mouth of each with a lighted match. (*c*) Add a drop of phenolphthalein indicator to each.

Observations: (*a*) Hydrogen is rapidly evolved. $Ca(OH)_2$ precipitates. (*b*) Pop, water forms. (*c*) Phenolphthalein turns red, indicating bases have formed.

Reference: Lapp, W. S., *J. Chem. Educ.*, **29**, 611 (1952); Weaver, E. C., *ibid.*, **24**, 48 (1947); Barnard, A. J. Jr. *et al.*, *ibid.*; Soroos, H., *Ind. Eng. Chem., Anal. Ed.*, **11**, 657 (1939).

2. FROM METAL PLUS STEAM

Dem. 69—Mg + steam

To show: Generation of hydrogen from Mg + steam. $Mg + H_2O \rightarrow MgO + H_2$.

Materials: Cell G-3, soap-bubble solution, granular Mg, $1 \times 1\frac{1}{2}$ in. asbestos tape.

Procedure: Fill the test tube of G-3 one-quarter full of granular Mg. Roll the asbestos tape lightly, wet it thoroughly, and push it into the tube so it rests on top of the Mg. Fill trough G-3 to the top with the soap solution. Project. Heat the Mg.

Observations: The burner heats the Mg red-hot and at the same time liberates steam from the wet asbestos. Masses of H_2 bubbles form in the trough. They can be ignited frequently with a lighted match.

Note: By adjusting the height of the soapy water it is possible to generate single hydrogen bubbles, which project beautifully.

Reference: Peterkin, J. D., *J. Chem. Educ.*, **11**, 481 (1934).

3. FROM METAL PLUS AN ACID

Dem. 70—Zn or Mg + Acid

To show: The generation of hydrogen from the interaction of zinc or magnesium with dilute acids.

Materials: Granular zinc, magnesium ribbon, dil.

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HCl, dil H_2SO_4, dil. acetic acid, cell C-g2(SD-7).

Procedure: Place Zn in each of three culture tubes, project, and add quarter of a tube-full of acid to each. Repeat using Mg ribbon. Test with a lighted match.

Observations: Hydrogen is generated in each case, and explodes with air.

Dem. 71—Zn + HCl: Effect of Acid Concentration

To show: The effect of HCl concentration in acting on zinc.

Materials: Granular zinc, dil. HCl, C-g2(SD-7).

Procedure: Place an equal number of grains of zinc in culture tubes. Project. Cover one with a quarter tubeful of water. Now add a quarter tubeful of dil. HCl to each, momentarily stirring the one containing the water.

Observation: The more concentrated solution reacts more vigorously.

Dem. 72—Zn + HCl: Effect of Grain Size

To show: The effect of grain size of zinc on its reaction with HCl.

Materials: Mossy Zn, HCl-dil., zinc 10 and 50 mesh; cell C-g2(SD-7).

Procedure: Place equal amounts of zinc in three culture tubes. Pour half a tubeful of dil. HCl into each.

Observation: The finer mesh zinc reacts much faster than the mossy zinc.

Dem. 73—Zn + HCl; Effect of Catalyst

To show: The couple-effect of Co^{++} or Cu^{++} on the reaction of zinc with HCl.

Materials: Mossy zinc, $CoCl_2$-aq., $CuCl_2$-aq., cell C-2g(SD-7), dil. HCl.

Procedure: Place equal amounts of mossy zinc in three culture tubes, about 1 g. each. Project. Half-fill with dil. HCl. Now to tube 2 add 1 ml of $CoCl_2$-aq., and to tube 3 add 1 ml of $CuCl_2$-aq., sufficient to color each tube.

Observations: The reaction is slow until the Co^{++} and Cu^{++} have been added; the Zn/Cu and Zn/Co couples accelerate reaction.

Notes: *1.* Cell C-3 can be used instead.
2. If reaction in tube 1 is too fast, dilute the acid.

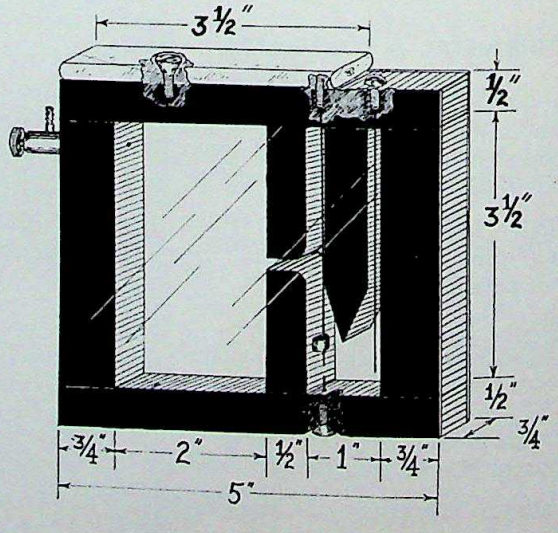
SUPPLEMENTARY DEVICES

SD-11—Electrolysis-Explosion Cell

This device was developed by Kimball A. Milton and his teacher George Frye of the Port Townsend, Washington, High School working with the author at the Science Theater Laboratory, U. S. Science Exhibit, Century-21, Seattle, 1962.

Construction of SD-11. Follow dimensions carefully. (*a*) The electrodes are made by boring holes and soldering, into two machine screws, $2^3/_4$ in.-long No. 22 platinum wires. The top plastic plate then has two holes bored and threaded to receive these screws. After screwing them two-thirds the way in from the top of the plastic plate, Plexiglas cement them so as to cover the solder joint, leaving only the Pt wire exposed on the underside of the plastic top. The lower end of the left electrode passes through a hole in a tiny piece of plastic, serving to hold the electrode rigid for sparking. (*b*) The upper end of the left electrode is soldered to the $^1/_4$-in. brass top-plate which serves as a ground during the sparking cycle. (*c*) The lower plastic plate carries a machine screw made flush with the bottom. During the sparking cycle the leak tester will be touched to this. (*d*) The chambers in which $2H_2$ and O_2 will be generated should both be $^1/_4$-in. wide. (*e*) The breach in the wall is rounded to facilitate emptying out gases. (*f*) It was found necessary to have the escape valve on the left wall, otherwise pressure builds up during electrolysis; in the subsequent discharge air from the larger chamber would surge into the small chamber. (*g*) Fill with 2 Normal H_2SO_4 solution.

Procedure: (*a*) Project the cell in position for electrolysis. Unscrew, opening the valve on the side-arm. Bring a phone-jack delivering 6 to 20 volts to the top contacts on the cell: gas commences to form at once. Stop when the $^1/_4$-in hydrogen chamber is about one-third full. Call attention to the fact that twice as much hydrogen as oxygen has formed. (*b*) Now close the side-tube by screwing the valve shut. With a quick motion, which requires practice, flip the cell completely over so as to bring the air to the other side of the large cell, and the hydrogen and oxygen together in the smaller cell. Again project. Bring a Tesla coil leak-tester to the spark-gap screw. A violent flash occurs, and the gases entirely combine to form water. (*c*) The cell is now ready to repeat the electrolysis-explosion cycle.



SD-11

(To be continued in May)

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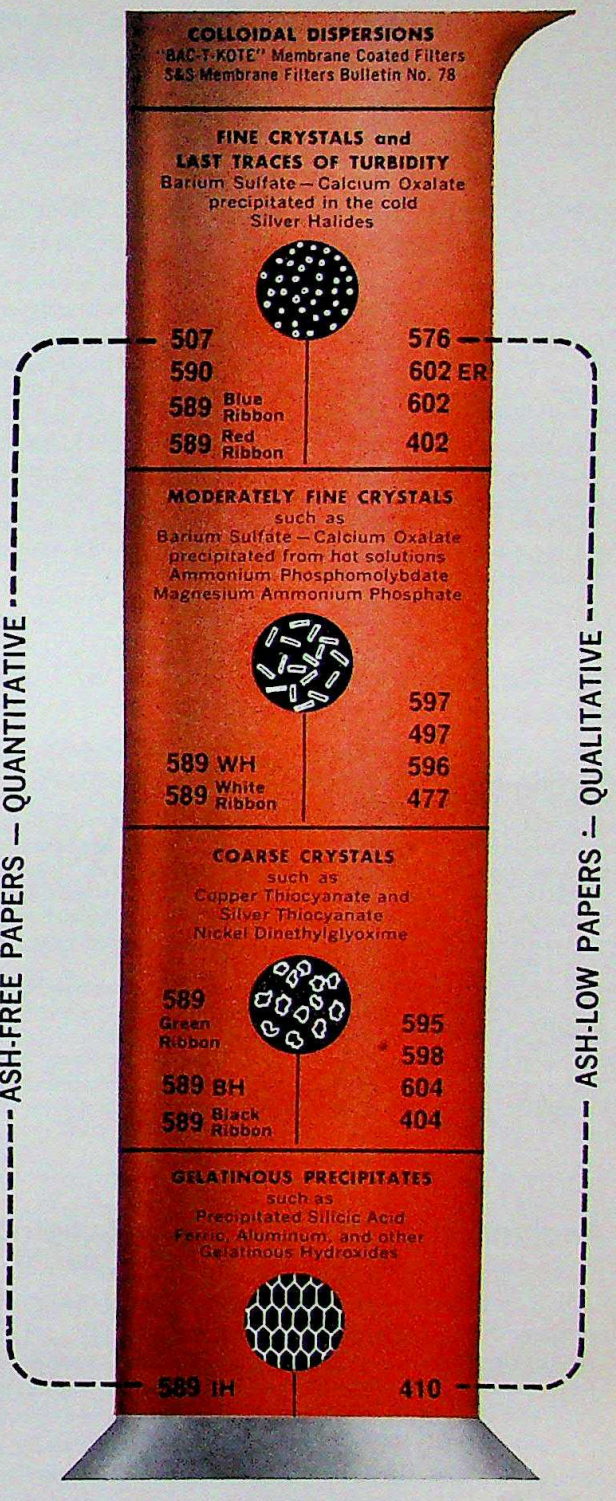
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CHEMICAL PROJECTS

Research Ideas for Young Chemists

Compiled by **JAY A. YOUNG**, King's College, Wilkes-Barre, Penna.
JOHN K. TAYLOR, National Bureau of Standards, Washington, D. C.

Precipitation from Homogeneous Solution

See GORDON, L., AND SALESIN, E. D., *J. Chem. Educ.*, **38**, 16 (1961).

The particles of a precipitate formed by mixing solutions of two reagents often exhibit different physical properties, depending upon the manner of mixing of the two liquids. In general the more slowly the liquids are mixed, the larger the particles of precipitate which form. It is possible in many instances to generate the precipitating reagent within the solution containing the component to be precipitated. In these cases the effect is similar to that which would be produced by very slow mixing of two solutions in the conventional way. Usually precipitates formed by this process have large, well-defined crystalline structures and in general are much more suitable for the purposes of quantitative analysis.

The precipitation of nickel dimethyglyoximate from homogeneous solution is described in the article.

Questions:

Suggest a reason why the onset of precipitation of nickel dimethyglyoximate should be delayed when the *p*H is changed from 7.9 to 7.1. Test your hypothesis by further laboratory work.

Devise a procedure for the precipitation of another substance from homogeneous solution. What factors which you can control in your procedure affect the properties of the precipitate or the onset of precipitation? Account for some or all of these effects and test your hypotheses by further laboratory work.

The Turbidimetric Determination of Lead

See PERKINS, G., JR., ET AL., *J. Chem. Educ.*, **38**, 358–60 (1961).

The quantity of precipitate in a turbid suspension can be determined by comparison with a turbid suspension of equal volume containing a known amount of precipitate, using a colorimeter or spectrophotometer. In this analytical procedure care must be taken to insure that the particles of precipitate are of approximately the same size in both the unknown and in the standard suspensions. In some cases these necessary precautions are effected by an elaborate time consuming procedure, but in the analysis described in this article these have been minimized.

In addition to the usual reagents and apparatus available in any laboratory, a Duboscq colorimeter or more elaborate electronic instrument will be required. A suitable substitute device could be designed by an ingenious student: essentially, a light source, a test tube holder, a barrier layer photo-cell, and a sensitive ammeter—all but the latter enclosed in a light tight box—would suffice.

Questions:

Devise a turbidimetric procedure for the determination of any suspended precipitate, other than lead molybdate.

Can you modify the procedure given in the article in order to obtain results with lower per cent errors than those reported? For example, precipitation from homogeneous solution, in which the particle size is controlled by regulation of *p*H or of the concentration of selected reagents, might be suitable; see L. GORDON AND E. D. SALESIN, J. CHEM. EDUC., **38**, 16 (1961) for introductory details.

When the absorbancy of a turbid suspension is plotted against concentration of precipitate, a straight line is not obtained; the data do not follow Beer's law. Can you account for the deviation from Beer's law? Test your hypothesis by further laboratory studies.

Analysis of Aspirin: A Conductometric Titration

See PROCTOR, J. S., AND ROBERTS, J. E., *J. Chem. Educ.*, **38**, 471 (1961).

Unlike most titrations, in a conductometric titration it is not necessary to stop adding titrant at the end-point. The end point is determined by a graphical analysis of the conductance of the titrated solution versus volume of titrant added over a range which includes data obtained both before and after the end point is reached. Also, no indicator is required. As usually performed, however, the procedure is tedious, since several conductometric measurements must be made.

But by using an inexpensive capacitance tester, available in kit form from well-known suppliers of electronic kits, the measurements may be quickly and easily performed and the desired analysis completed by a graphical analysis of the data. In the article, the procedure for a conductometric determination of aspirin is described.

Questions:

Select other available substances, instead of aspirin, and determine the amount, or concentration, present by a conductometric titration. Suggested common substances are vinegar, baking powder, other pharmaceutical products in addition to aspirin, rock salt, and other household materials.

Can you use a conductometric titration to assist in the solution of a problem listed in another project in this series?

The authors suggest that the potentiometer furnished with the capacitance tester kit is not strictly linear, at least at the extreme ends of the winding. Is this true for your tester? If so, do you think it would be desirable to replace the potentiometer which is furnished with a more precisely linear potentiometer? Support your conclusion with data obtained in the laboratory.

NOTE: This project is particularly recommended to students who are interested in electronics and its relation to the experimental study of chemistry.

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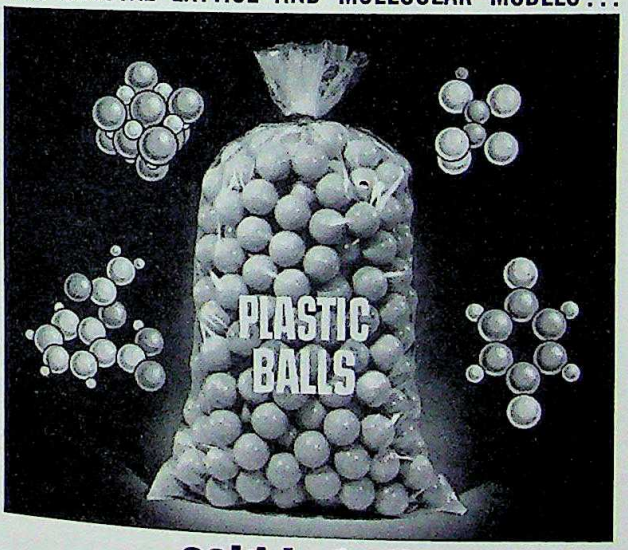
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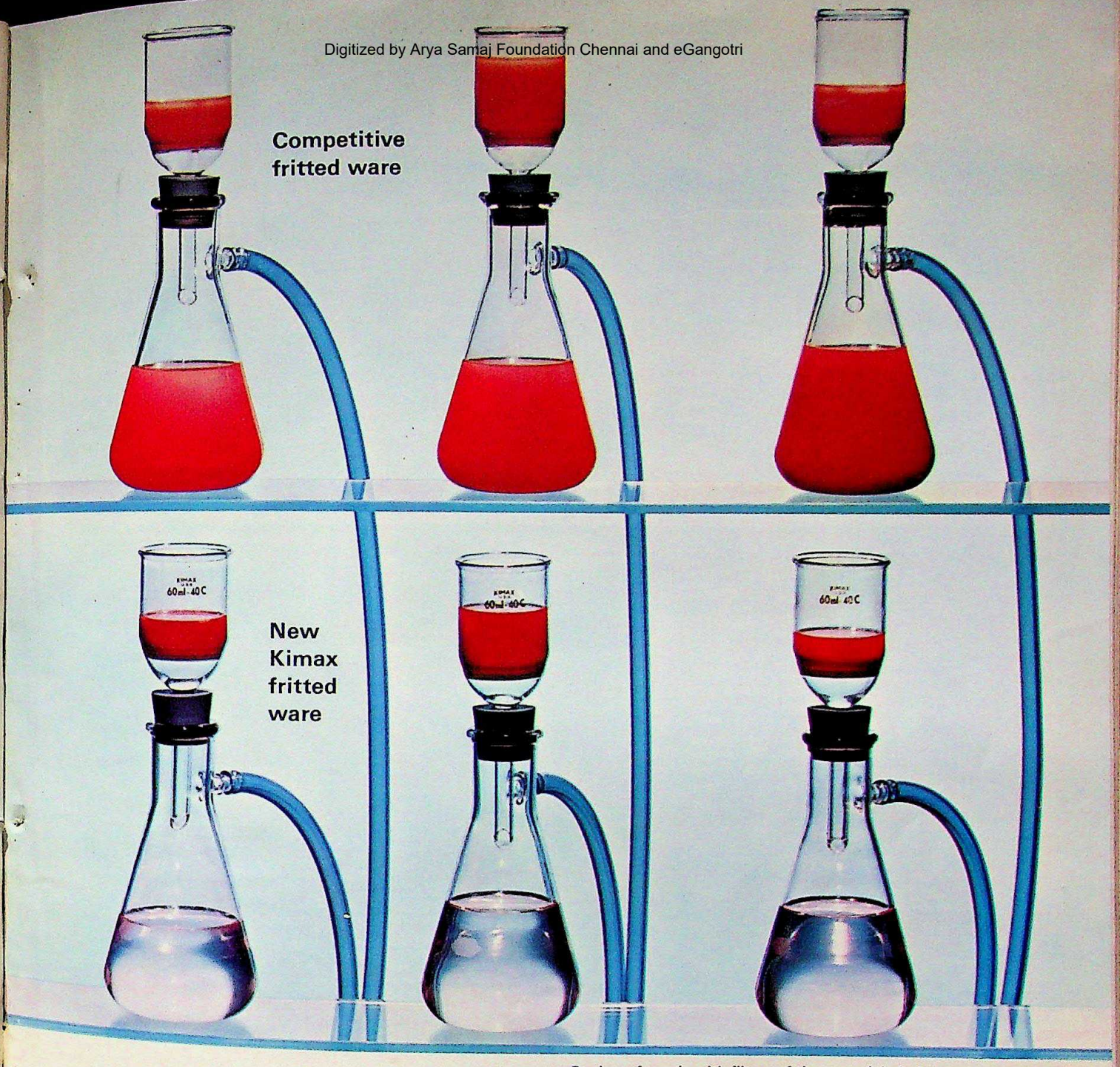
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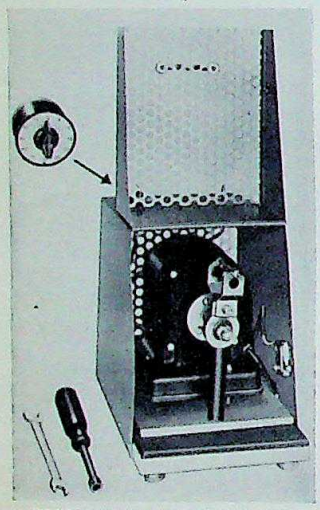
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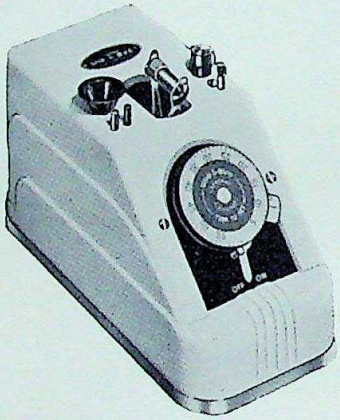
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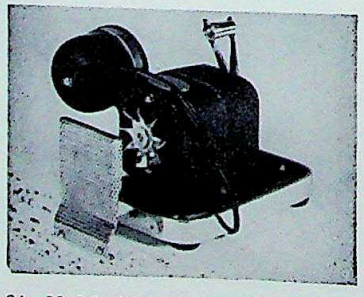
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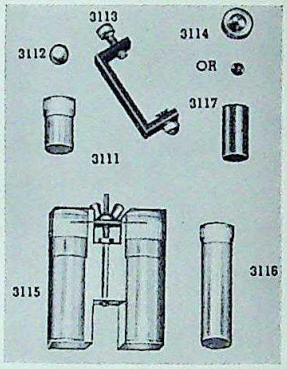
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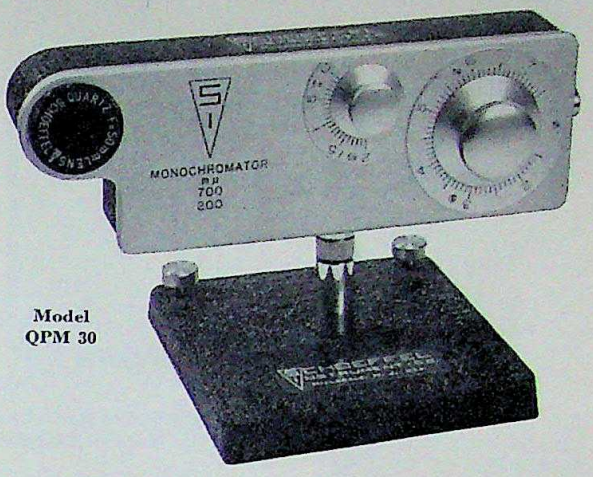


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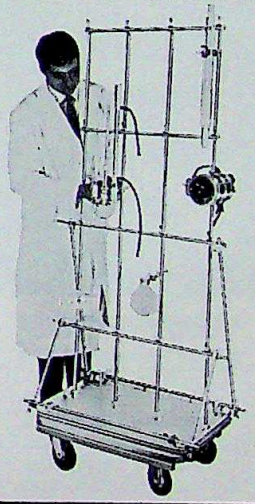
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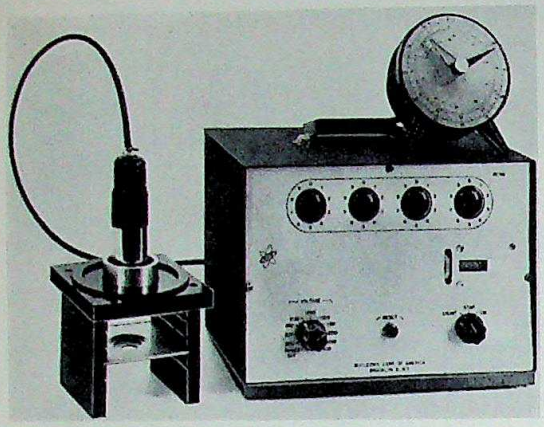
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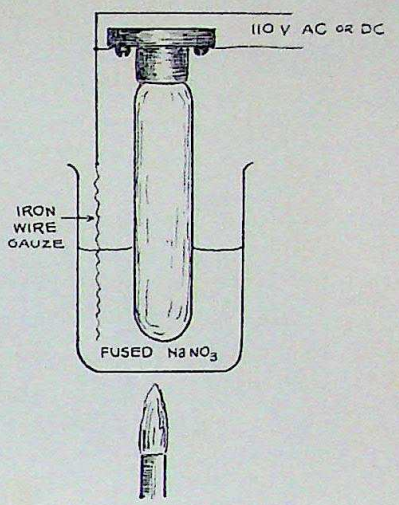
ELECTROLYSIS OF SODIUM THROUGH GLASS

A Chem Ed TESTED DEMONSTRATION

Rewritten from: D. K. Alpern, THIS JOURNAL, *34*, 289–90 (1957) by F. B. Dutton
Checked by: Joseph E. Bowles, Oak Ridge Institute of Nuclear Studies

PREPARATION

Assemble a 25 watt tubular electric lamp, socket, iron wire gauze, and provision for connection to 110 v ac power source as shown in diagram. Provide a 250 ml beaker containing melted sodium nitrate and burner to maintain temperature just above the melting point (308 °C) as shown.



DEMONSTRATION

Lower lighted bulb and iron gauze assembly into molten salt. Maintain temperature just high enough so the surface of the molten salt does not freeze (*ca.* 350 °C). Sodium metal will be deposited on the inside of the bulb at the upper cooler region.

CAUTION

Care should be taken to use clean equipment and materials. Fused $NaNO_3$ is a vigorous oxidizing agent. Avoid contact with combustible material. Operate over a fireproof table surface.

REMARKS

The bulb containing a sodium mirror may become a permanent demonstration item to show students the appearance of a clean sodium surface.

dc may be used in which case the Fe anode must be connected to the positive lamp terminal. This is a versatile demonstration which may be used in connection with discussion of electron emission from a hot filament, rectification, Faraday's law, the structure and conductivity of glass, photoelectric devices, and the commercial production of metals from fused salts—see reference given as the source of this demonstration.

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EFFECT OF CHLORIDE ION ON PRECIPITATION OF CADMIUM SULFIDE

A Chem Ed TESTED DEMONSTRATION

Submitted by: T. A. O'Donnell, The University of Melbourne, Australia.
Checked by: R. B. Escue, North Texas State College, Denton, Texas.

PREPARATION

Prepare a suspension of CdS by adding 1 ml 1 *M* $Cd(NO_3)_2$ solution and 5 ml H_2S saturated water to 200 ml of 2 N (1 *M*) H_2SO_4. Pour into identical flasks 100 ml volumes of the suspension. Provide 0.1 mole of solid NaCl (5.85 g) or KCl (7.46 g) and 0.1 mole of corresponding nitrate (8.5 g or 10.1 g).

DEMONSTRATION

Add 0.1 mole of solid NaCl or KCl to one flask and 0.1 mole of corresponding nitrate to the other flask. The suspension which has been made 1 *M* in Cl^- ion, will disappear while the other suspension will remain unchanged.

REMARKS

Frequently when the precipitation of cadmium sulfide from hydrochloric acid solution is discussed the usual treatment is to deal with the effect of *p*H on the concentration of free sulfide ion. Only rarely is the effect of the chloride ion discussed quantitatively or qualitatively. In each case, the acidity and ionic strengths are the same, the only difference between the two systems being that the solution in which the cadmium sulfide dissolves is 1 *M* in chloride ion. The sulfide dissolves because ionic equilibria involving entities such as $CdCl_4^{2-}$ must compete with the *p*H-dependent equilibrium between cadmium ions, sulfide ions, and solid cadmium sulfide.

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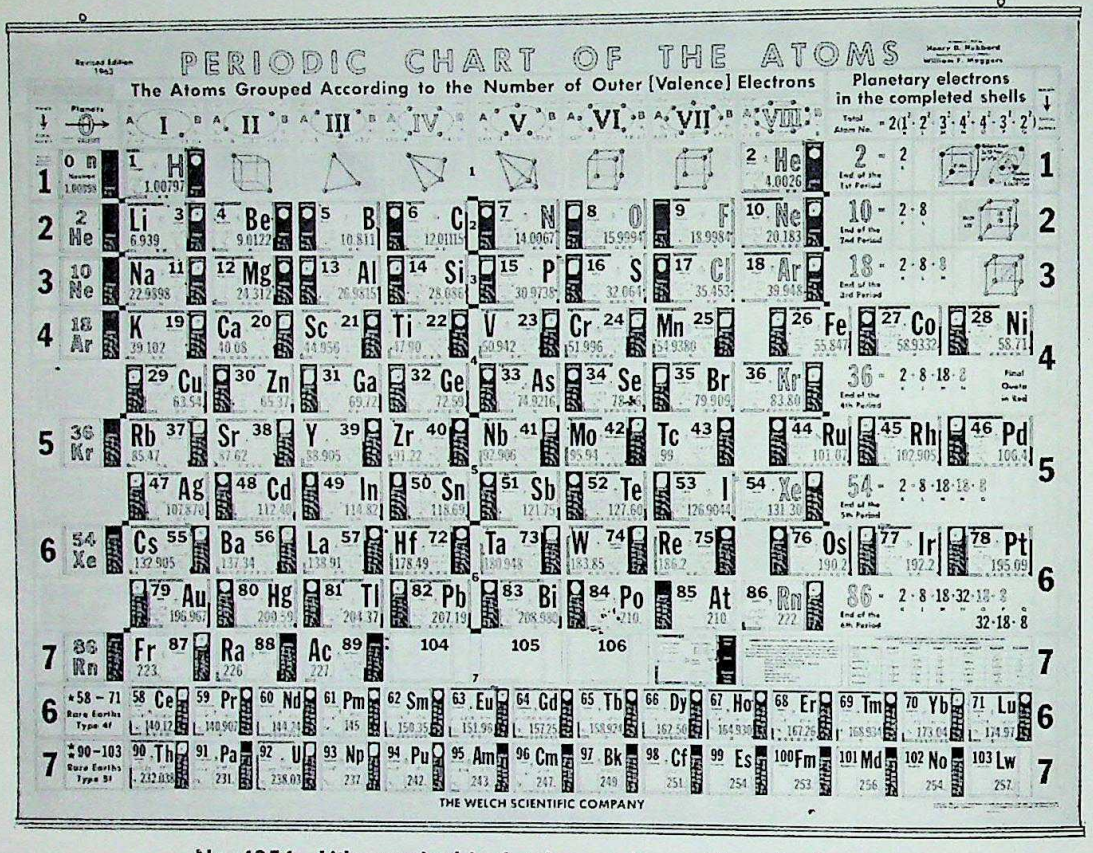
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Chem Ed

EDITORIALLY SPEAKING

EDITOR'S NOTE: It is most appropriate for an issue devoted mainly to the chemistry of the sixth element to begin with a sermon preached on the same text. Fortunately for the non-organic editor, the following version of Dr. Lambert's provocative discussion at the Atlantic City Meeting was available. The author once before appeared at an Atlantic City ACS Meeting with a trunkfull of brightly colored styrofoam (see THIS JOURNAL, **34**, 217 (1957)). This time his language was equally brilliant. We enthusiastically (and gratefully!) devote this page to "Effective Teaching of Organic Chemistry."

Effective Teaching of Organic Chemistry

Throughout the country there is a stimulating ferment brewing in the teaching of organic chemistry. But the ferment consists principally of new content and the reorganizing of content: emphasis on mechanisms and principles, recasting of traditional functional group reactions into more meaningful patterns of mechanistic types. I believe that the brew is being cooked in too ancient a kettle.

Subject matter revisions, mild or revolutionary, are not enough. The techniques by which the subject matter is presented to the student sadly need our attention—and the easiest technique to improve is the organic lecture.

The standard lecture system is obsolete in organic chemistry classes smaller than 125 students. Why do instructors ignore the contribution of Johann Gutenberg to chemistry? Thanks to him, we now have movable type! A few chemists can write books which are readable. Why then do we fail to use these excellent modern texts as the principal bases for our courses?

The educational waste involved in the traditional process of writing coveys of equations on a blackboard while the student frantically re-copies them incorrectly in his notebook before they are shot down by an eraser should be apparent to most of us. An old gag involves the professor who writes with his right hand while erasing with his left; it is an old gag, but it is not funny if we are interested in education rather than boardmanship—and that last word can be spelled in two ways.

Lecture time is too valuable to waste in outlining a textbook; yet astonishingly few instructors employ any other technique in their lectures. Perhaps it is because we tend to reserve our problem-solving capabilities for laboratory research rather than to apply a modicum of them in discovering how to teach a class of students. Two better variants can be devised.

Certainly these suggestions are too obvious to be original. They are just not widely applied. Robert Levine, in a paper describing the teaching of organic chemistry at the time of the ACS diamond jubilee (see THIS JOURNAL, **29**, 224 (1959)), quotes a letter from Professor Ray Brewster of Kansas in which he describes his use of this technique. My experience of auditing organic chemistry classes as a NSF faculty fellow in 1958, however, convinces me that there are few who use such approaches to presenting the material. In my travels to major institutions across the country, there were 37 conventional, dull lectures out of the 40 visited. If I had been a bird watcher, I could have made quite a collection: "White-chested monotones," "addle-pated note watchers," and "unprepared cocky-crested high fliers," to mention a few.

If the large Noller or the large Fieser, or similar comprehensive book is used as a reference text, the lectures should be mimeographed verbatim and issued to the students at the start of the course. The students should be required to read over the lectures and do problems in advance of the lecture period. The large reference book is specifically referred to in the mimeograped lectures for expansion of points of further information on difficult areas.

What becomes of the lecture period in such a system? Even if it cannot always be transformed into a successful question-and-answer period, it can at least be a much more meaningful discussion of examples of the most difficult parts of the lecture assignment. (In the name of Gutenberg, let us not read our mimeographed lecture notes to the class! I have actually seen that done.)

Some may prefer a second variant which involves choosing a completely readable textbook, one in which all or almost all of the material will be read and studied by the student in the course of a year. A few of the many possible examples would include Cason, Geissman, Morrison and Boyd, and English and Cassidy. The text should be not only readable but replete with problems, preferably mixed in with the material rather than at the ends of the chapters. Answers to all problems must be supplied either in the text or by the instructor. Then, if the student is issued a detailed

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syllabus of the text in which less important sections are *labeled as such* and the most important sections are underscored, we have the "Gutenberg teaching-machine"—the poor man's programed instruction. Surely, all the elements of self-instruction, programed instruction, are there:

Active Engagement of the Student. He knows this section is going to be discussed, not outlined, at the next lecture and that he will be lost if he doesn't study the 8–12 readable pages in the assignment.

The System is Self-pacing. The student can go as rapidly as he wants—and turn to other sources such as Noller, Cram, Gould, or Hine, if he is a fast man. On the other hand, an absolutely minimal list of problems is given for the slower individual to conquer.

The Material is Presented in Small Steps. There is immediate feedback if there are enough problems after every section or series of paragraphs. Every problem has an answer. The student himself can find his own errors and determine his weaknesses. Admittedly, no text is the complete equal of a psychologically-designed, programed instruction course, but this system comes closer than the use of most texts alone.

Now the lecture, as in the first variation, becomes a discussion session, but even more successfully because the text or syllabus has more problems. As a result the students come to class with questions, or at least ready for the instructor to pose questions. What a revolutionary experience it is to teach such a class!

The usual lecture is a desperately sad affair, viewed objectively. The instructor presents a boardful of logically-organized material with answers by the score, beautiful answers—to questions that the students have not asked. What is more futile than that?

In a modern "Gutenberg" lecture, things still do not work perfectly, of course. The students are not used to pre-studying before the day of the lectures. It is against all of their previous training and their other course practices. A few just do not do the work that they should, hoping to catch something from the lecture, or to regain skipped ground just before the next exam. No, of course, it does not work perfectly, but it works excellently for the A and B students. I believe that it does for the C people as well, because at all levels the student gets the feeling that here at last is a course in which he is involved. The burden for his achievement is directly and immediately on him, as he reads the text and tests himself with problems. The instructor's role is changed from that of a "high-priest of science," droning on in endless lectures, to that of a "coach" in the highest sense—a mentor who is concerned with showing the student ways to become proficient in a new and challenging field.

Our job is to aid students to learn—not to impress them with our skill at blackboard writing. We can not do it without content—or without techniques which involve the students in the struggle to stretch their own minds.

Frank L. Lambert
Occidental College
Los Angeles, California

Project Syntheses for Organic Laboratory Courses

Prof. Stanley C. Bunce of Rensselaer Polytechnic Institute, Troy, N.Y., has provided the following list of compounds which experience has shown to be suitable for assignment in the elementary organic laboratory course (see Abstracts of Papers, 142nd Meeting ACS, p. 4F). Since the effectiveness of the assignment depends on the student's learning the literature sources, these are not given. They will be supplied by Dr. Bunce to interested professors on request.

Compound	Steps in Synthesis	Difficulty[a]
Adrenalin	3	D
2-Amino-4-chlorothiophenol	3	A
Aminomalonamide	3	A
3-Aminopicolinic acid	4	D
Benzedrine	2	D
Biphenylene	4	D
N-Bromomethylphthalimide	2	E
2-Carboethoxycyclopentanone	2	A
4-(4-Carboxyphenyl)semicarbazide	3	A
3-Chloro-2-bromotoluene	4	D
γ-Chlorocrotonaldehyde	2	D
2-Cyanopyridine	3	A
Cyclobutyl methyl ketone	4	D
Cyclopentanecarboxylic acid	3	A
Cyclopropanol	2	D
2,3-Diaminopyridine	1	D
3,3′-Dichlorobenzidine	2	A
Dichloromaleic anhydride	2	A
5,8-Dichloroquinoline	1	A
Diethyl aspartate	1	A
Diethyl α,α′-dibromoadipate	2	D
1,5-Difluoronaphthalene	3	A
Dimethyl-*p*-acetylphenylcarbinol	3	A
N,*N*-Dimethylaminobutyric acid	3	A
Dimethylcyclopropylcarbinol	2	A
2,4-Dinitrobenzenesulfenyl chloride	2	A
1,5-Diphenyl-3-pyrazolecarboxylic acid	3	A
1,1-Diphenyl-2-trinitrophenylhydrazyl	2	A
Diphenylguanidine	2	A
Ethyl β-aminopropionate hydrochloride	2	A
Ethyl *N*-phenyloxanilate	2	A
Ethyl nitroacetate	2	A
Ethylurea	3	A
2-Fluoronaphthalene	2	A
D-Glyceraldehyde	3	D
Hexane-3,4-dione	2	A
Hexaphenylbenzene	4	D
1,3-Indandione	2	A
1-Indanone	2	A
Isonicotinic acid hydrazide	2	A
p-Isopropylstyrene	3	D
Methylenecyclobutane	3	D
l-Menthyl *p*-toluenesulfinate	2	A
2-Naphthaldehyde	2	A
α-Naphthylisothiocyanate	2	E
m-Nitroanisole	2	E
5-Nitrosalicylaldehyde	2	A
6-Nitro-2-mercaptobenzothiazole	2	A
Phenanthridine	4	D
Phenobarbital	5	D
Phthalazine	2	D
Progesterone	3	D
Tetraphenylmethane	2	A
Tribiphenylmethyl	3	D
2,4,5-Trichlorophenoxyacetic acid	3	D
2,4,6-Trichlorophenoxyacetic acid	3	D
β,β,β-Triphenylpropionamide	3	E

[a] A = Easy; E = Difficult

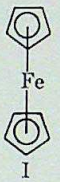
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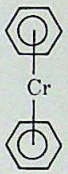
R. Pettit, G. Emerson, and J. Mahler
University of Texas
Austin

Chemistry of the Diene-Iron Tricarbonyl Complexes

One of the most rapidly developing areas of organic chemistry during the last few years has been the field of organo-metallic complexes. Several metals such as magnesium, sodium, lithium, and aluminum have long played very important roles in organic chemistry which are still being intensively studied; but the discovery of the so-called sandwich compounds, exemplified by ferrocene (I) and dibenzenechromium (II), has given a great impetus to the investigation of the organic chemistry of other elements in the periodic table, especially the transition metals. The interest



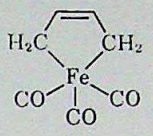
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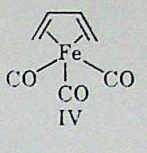
II

in such complexes stems from two main sources. First, the bonding in these complexes is quite complicated and much work has been done in trying to correlate physical properties with various models purporting to describe the electronic structure. Secondly, the chemical behavior of many such complexes has been found to be quite unique and is being actively studied by many research groups.[1] In this connection it might be mentioned that the catalytic role of metals in several important commercial synthesis, for example of cobalt in the oxo process, is now more clearly understood because of such studies (*1*).

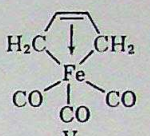
The paper presented here will describe results of experiments carried out at the University of Texas in a very limited area of this part of organic chemistry and is restricted to certain aspects of the chemistry of the diene-iron tricarbonyl complexes. Our early study was initiated by some work recently reported by Hallam and Pauson (*2*) relating to an almost forgotten reaction between butadiene and iron pentacarbonyl. This reaction was first reported in 1930 by Reihlen and coworkers (*3*) who found that butadiene and $Fe(CO)_5$, when heated together, formed a complex, $C_4H_6Fe(CO)_3$, for which they proposed (III) as a possible structural



III



IV

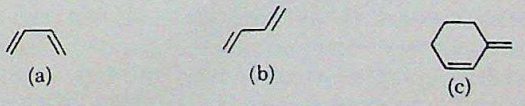


V

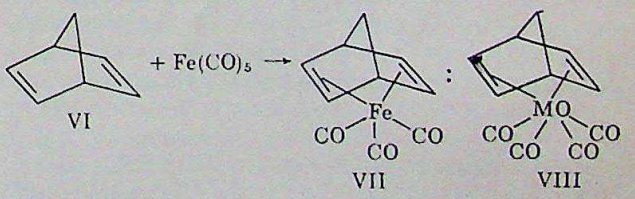
formula. Hallam and Pauson then later extended the series of compounds to other diene systems. Because of the unusual stability of the compounds and by analogy with ferrocene and other sandwich complexes the latter workers proposed (IV) as that best representing the bonding within the complex. It is implied in structure (IV) that the four carbon atoms of the diene system largely retain their sp^2 state of hybridization upon complex formation. The bonding of iron to the diene involves interaction of atomic orbitals of iron with the molecular orbitals of the diene as a whole rather than the terminal atoms alone as would be implied in (III). A third possible structure (V) was later brought forth for consideration, but then rejected on the grounds of certain spectroscopic data, by Wilkinson and coworkers (*4*). We shall consider the nature of the bonding in more detail at the end of this paper and shall continue to use the formula (IV) type representation.

Hallam and Pauson concluded from their study that the following two requirements must be met by the diene in order that it may successfully form diene-iron tricarbonyl complexes.

(1) The diene must be able to adopt a cisoid conformation. That is, the two double bonds can be arranged as in (*a*) rather than (*b*). The diene of structural formula (*c*) is thus not expected to form a stable complex.



(2) The double bonds of the diene must be conjugated. The former of these two suggestions appeared very reasonable but the latter was based on less sound arguments; and, in order to test its validity, the following reaction between bicycloheptadiene (IV) and $Fe(CO)_5$ was attempted. It is seen in this diene that the two



VI VII VIII

double bonds are not conjugated but nonetheless are so oriented in space that bonding to iron could conceivably occur. A reaction was indeed found to occur—the

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[1] Excellent reviews of various aspects of organo-metallic complexes are compiled in "Organo-metallic Chemistry," edited by H. Zeiss, Reinhold, New York, 1960.

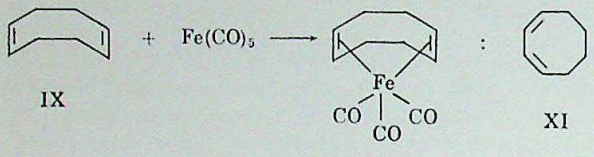
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product being bicycloheptadiene-iron tricarbonyl complex (VII). A similar reaction was also found to occur between (VI) and molybdenum hexacarbonyl, with production of the analogous complex (VIII). At the same time this work was reported Wilkinson and his collaborators (*5*) also demonstrated the unimportance of conjugation in these complexes by means of the identical reaction of $Fe(CO)_5$ and (VI) just mentioned.

Rearrangement of Dienes During Reaction with $Fe(CO)_5$

During experiments designed to extend the series of non-conjugated diene-iron tricarbonyl complexes to other diene systems a reaction was attempted between 1,5-cyclooctadiene (IX) and $Fe(CO)_5$ with the object of making the complex (X). On paper such a reaction

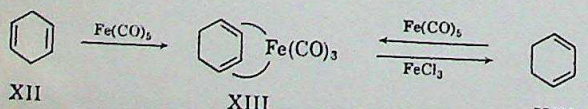


IX X XI

seemed feasible. However, no organo-metallic complex was found in the reaction mixture and most of the $Fe(CO)_5$ was recovered unchanged. Further investigation showed that the 1,5-cyclooctadiene had been quantitatively converted to the isomeric 1,3-cyclooctadiene (XI) with no trace of any other organic compound being detected. Control experiments have established that this unexpected isomerization is not merely a thermal reaction of the 1,5-isomer but that the $Fe(CO)_5$ must be playing some specific role. It has also been shown that only catalytic amounts of $Fe(CO)_5$ are required to effect the rearrangement. Bicycloheptadiene-iron tricarbonyl, and to a lesser extent osmium carbonyl, are also found to be catalysts but the carbonyls of chromium, nickel, tungsten, and molybdenum are completely ineffective under the same conditions (*6*).

A knowledge of the scope and mechanism of the above arrangement seemed desirable and our progress to date in this direction is reported here.

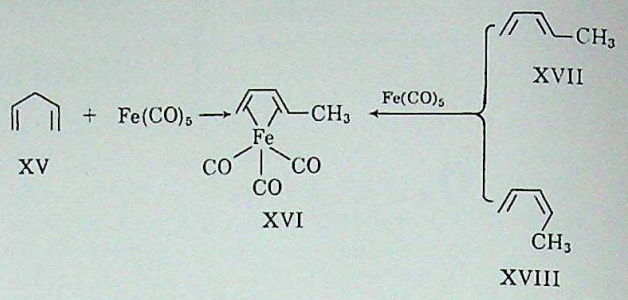
The rearrangement of non-conjugated dienes with $Fe(CO)_5$ appears to be fairly general, but the usual products of the reaction are conjugated diene-iron tricarbonyl complexes rather than the free rearranged dienes. For example, 1,4-cyclohexadiene (XII) reacts with $Fe(CO)_5$ to produce 1,3-cyclohexadiene-iron tricarbonyl (XIII), identical with the complex obtained from 1,3-cyclohexadiene (XIV) and $Fe(CO)_5$. The structure of the ligand in XIII was determined by decomposition with $FeCl_3$ and comparison of the liberated ligand with authentic material. This facile decomposition of such complexes has been found to be a very useful reaction for purposes of identifying the ligands. Similarly, 1,5-hexadiene gives rise to a mixture of 1,3- and 2,4-hexadiene-iron tricarbonyls.



XII XIII XIV

Three further examples which have possibly thrown some light on the mechanism of the reaction are shown below.

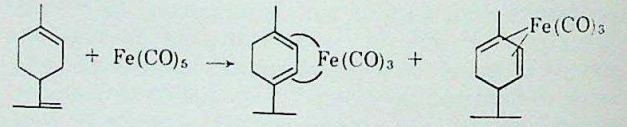
The reaction of 1,4-pentadiene (XV) with $Fe(CO)_5$ produces *trans*-1,3-pentadiene iron tricarbonyl XVI. This same product is obtained when either *trans*-1,3-



XV XVI XVII XVIII

pentadiene (XVII) or *cis*-1,3-pentadiene (XVIII) is reacted with $Fe(CO)_5$. In this last reaction a conceivable pathway of the reaction is first of all thermal isomerization of (XVIII) to (XVII) followed by reaction with $Fe(CO)_5$ to produce (XVI). However, this route must be ruled out because an independent study has shown that the rate of formation of (XVI) from (XVIII) and $Fe(CO)_5$ is *faster* than the thermal isomerization of (XVIII) to (XVII).

To introduce another complication, it has been shown that *d*-limonene (XIX) reacts with $Fe(CO)_5$ to give a mixture consisting of predominantly two organo-metallic complexes which probably have structures (XX) and (XXI), although this has not been established with certainty. The interesting point however is that the mixture displays no optical activity. Although the original center of asymmetry in (XIX) is probably de-



XIX XX XXI

stroyed during the reaction, both the complexes (XX) and (XXI) should be capable of existing in optically active forms and the product was therefore expected to be optically active.

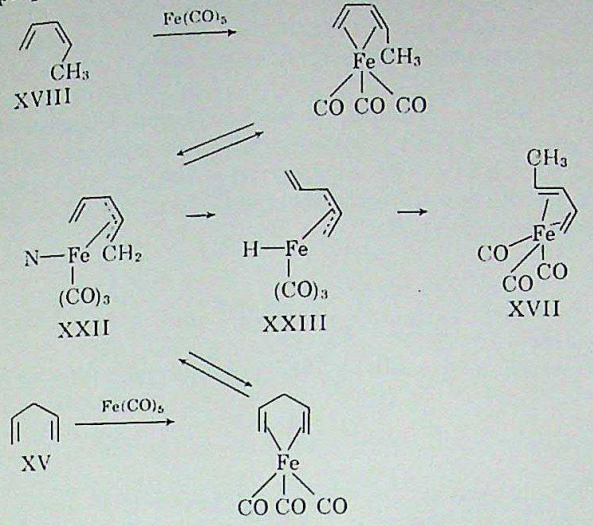
Finally, another observation, which probably has some bearing on the mechanism of the rearrangement of the dienes, is that mono-olefins also react with $Fe(CO)_5$, under the same conditions, to give isomerized products. Thus 1-octene reacts to give a complex mixture of 1,2,3 and 4-octene apparently identical in composition to that obtained from 2-octene under similar conditions. Other olefins also rearrange to give mixtures of olefins. It should be noted here that Asinger and Berg (*7*) had previously observed that 1-dodecene was isomerized to a mixture of compounds by heating with $Fe(CO)_5$; however, they did not pursue this further.

As to the question of the mechanism of the reactions, the experimental results obtained so far do not provide an unequivocal answer and further work in this direction is in progress. But sufficient data has been collected to at least allow us to postulate a possible pathway which can then be used for designing critical experiments. Taking the reactions of *cis*-1,3-pentadiene (XVIII) and 1,4-pentadiene (XV) with $Fe(CO)_5$ as

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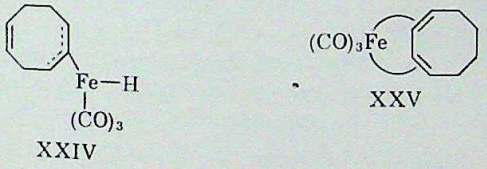
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examples, the following mechanistic pathways for formation of *trans*-1,3-pentadiene-iron tricarbonyl are proposed.



The essence of this proposal is that a diene iron tricarbonyl complex is formed, the iron atom of which can then abstract an allylic proton to form a π-allyl-hydro-iron-tricarbonyl (XXII) in which the olefinic double bond is now not attached to iron and is free to rotate into the more stable conformer (XXIII). The hydrogen transfer step is presumed to be reversible, the final product is then (XVI), which must then be the more thermodynamically stable complex isomer. An analogous scheme, also involving reversible allylic hydrogen abstraction by iron can also be written for the rearrangement of mono olefins, the first step being formation of an olefin-iron carbonyl complex.

A similar scheme involving stepwise formation of intermediates such as (XXIV), can also explain the

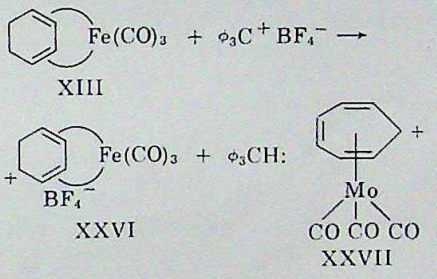


catalytic isomerization of 1,5-cyclooctadiene, the only additional postulate required is that the 1,3-diene-complex (XXV) reacts irreversibly with 1,5-cyclo-octadiene to form 1,3-cyclooctadiene and the 1,5-diene-complex which then undergoes further isomerization. This exchange is consistent with the fact that bicycloheptadiene-iron tricarbonyl catalyzes the reaction and also with the optically inactive product obtained from the reaction of *d*-limonene with $Fe(CO)_5$ mentioned previously. The thermodynamics of the over-all reaction is also consistent with the fact that 1,3-cyclooctadiene is more stable than the 1,5-isomer by 4.7 kcal, as determined by heats of hydrogenation.[2] Further experimental work, designed to test the above suggestions, is now in progress.

Chemical Behavior of the Diene-Iron Tricarbonyl Complexes:

An interesting question to ask concerning these diene complexes is the following. How does the organic chemistry of conjugated dienes, while bonded to the $Fe(CO)_3$ group, compare to that of the free diene itself? It turns out that the behavior of the two are quite different. Hallam and Pauson have already shown (*2*) that butadiene-iron tricarbonyl can not be induced to undergo Diels-Alder reactions, is unreactive towards catalytic hydrogenation, and, furthermore, that the material can even be recovered unchanged from solutions in concentrated sulfuric acid. Generally the dienes are then much less reactive in the complexed form.

However, there is at least one reaction in which the complexed form of the diene reacts more readily than the free diene itself, this involves the abstraction of a hydride ion on a carbon atom adjacent to the diene-linkage. With certain diene-iron tricarbonyl complexes such an abstraction can take place with surprising ease. Thus Fischer and Fischer (*8*) have found that reaction of cyclohexadiene-iron tricarbonyl (XIII) with triphenylmethyl tetrafluoroborate produces cyclohexadienylium-iron tricarbonyl tetrafluoroborate (XXVI) and triphenyl methane. Dauben and Honnen (*9*) had previously used this reaction to produce the tropylium-molybdenum-tricarbonyl cation (XXVII) from cycloheptatriene-molybdenum tricarbonyl. Several other salts of the type (XXVI) are now known, though not all have been made using this method.



The driving force for the hydride abstraction reaction stems largely from the stability of salts of the type (XXVI). At first sight it may seem surprising that a carbonium ion can formally act as a ligand to give stable complexes.

However, according to current concepts[1] a very important electronic interaction in such systems, and in metal carbonyls in general, involves back donation of electrons from the central metal atom into unoccupied molecular orbitals of the ligand. The conjugated carbonium ion ligands in the above salts possess low-energy unoccupied molecular orbitals suitable for strong bonding via back donation.

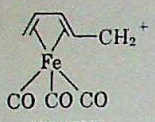
The cationic complexes are remarkably resistant to nucleophilic attack as is evident from the fact that they often may be recrystallized from water.

All of the cationic complexes reported in the literature have cyclic carbonium ions as ligands. An interesting stereochemical question now arises in the case of similar complexes having acyclic carbonium ion as ligands, namely do they exist and if so can they exist in isomeric pairs as illustrated in formulas (XXVIII) and (XXIX)? In each case the pentadienyl cation possesses a low lying, vacant molecular orbital favorable for strong bonding by means of back coordination, but in the *trans* isomer (XXVIII) the Fe atom cannot be bonded to the five sp^2 carbons of the dienyl ligand simultaneously, whereas in the case of the *cis* isomer (XXIX) it conceivably could be.

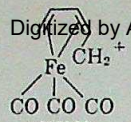
[2] Personal communication from Professor R. B. Turner.

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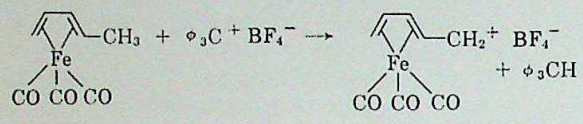
XXVIII



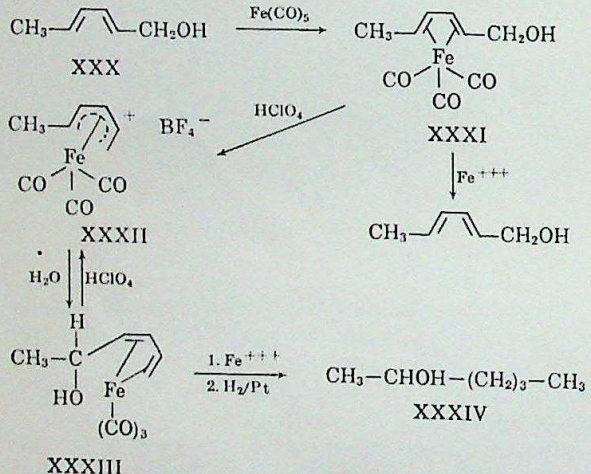
XXIX

No linear ligands of the type in question were known at the time so an investigation into this series of complexes was undertaken.

We have been uniformly unsuccessful in our attempts to prepare linear carbonium ion complexes of the type in question by hydride abstraction from *trans* substituted diene-iron tricarbonyls by the Dauben method as indicated in the following reaction.



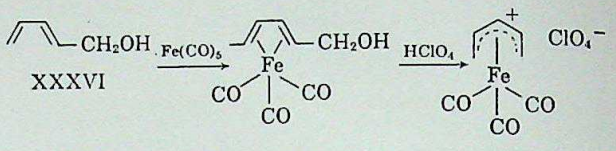
However acyclic pentadienyl iron tricarbonyl cations have been successfully prepared from the corresponding alcohols by the method indicated in the following sequence (*10*). As shown *trans-trans*-2,4-pentadiene-1-ol (XXX) reacts with $Fe(CO)_5$ to give the usual diene-



XXXIII

iron tricarbonyl complex (XXXI). Reaction of this product with iron (III), ion regenerates the starting alcohol, indicating that no isomerization has occurred during its formation. Reaction of the alcohol complex (XXXI) with $HClO_4$ produces a nicely crystalline salt, which, from analysis and other data, is found to be the fluoroborate salt of the desired acyclic complex cation (XXXII). However it should be noted that in formula (XXXII) the five sp^2 carbons are now assigned an all cisoid configuration. The reason for this assignment is as follows. As indicated in the above scheme the salt reacts with water to produce a new dienol-iron tricarbonyl complex (XXXIII) which also reacts with perchloric acid to regenerate the salt. Decomposition of the complex (XXXIII) followed by reduction gives 2-hexanol. Now since only dienes in their cisoid conformation can be complexed to a $Fe(CO)_3$ group, the structure of the new alcohol complex must be as indicated by (XXXIII) in which, it should be noted, carbon atoms, 1 and 4 are now cisoid with respect to the 2,3 bond whereas in the original alcohol (XXX) they were in a *trans* relationship. Obviously then a geometrical inversion has occurred and the most likely place appears to be during the reaction of the alcohol (XXXI) with $HClO_4$ with formation of the salt (XXXII). The reason for the inversion apparently being the increased bonding available when all five sp^2 carbon atoms are cisoid.

In a similar manner, pentadienyl-iron tricarbonyl perchlorate (XXXV) is produced from *trans*-pentadieneol (XXXVI). By analogy with the previous case we write the five sp^2 carbons to again have the all cisoid configuration as shown.



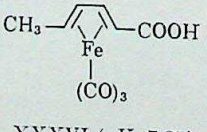
XXXV

The problem as to whether the analogous "*trans*" cations, exemplified by XXVIII, can exist as stable entities or not so far remains unanswered and further experimental work will be required for its solution.

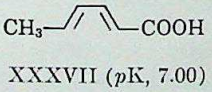
The Electronic Effects of the Diene-Iron Tricarbonyl Group

Another aspect of the chemistry of this class of compounds which we have briefly studied is the nature of the electronic effect of the diene-iron tricarbonyl system when considered as a substituent group. Although only limited data is thus far available it appears that the general electronic effect of the group is one of electron donation.

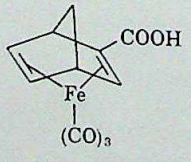
Thus hexadienoic acid-iron tricarbonyl (XXXVI) is a slightly weaker acid than hexadienoic acid itself (XXXVII). Likewise bicycloheptadiene carboxylic acid (XXXIX) is a slightly stronger acid than when complexed with $Fe(CO)_3$ (XXXVIII). The pK's for these systems (determined in ethanol-water mixtures) are indicated in the following formulas. It is interesting to note that the opposite effect has been found for



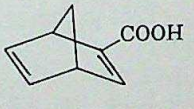
XXXVI (pK, 7.25)



XXXVII (pK, 7.00)



XXXVIII (pK, 7.50)



XXXIX (pK, 7.00)

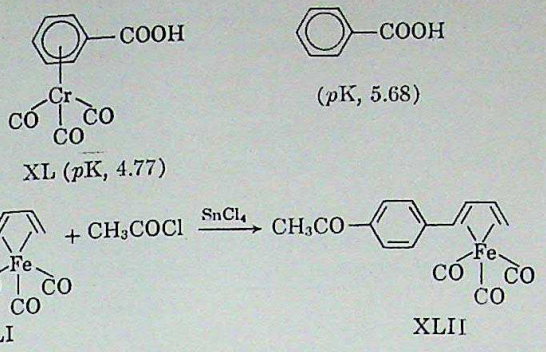
the aryl-chromium tricarbonyl group (*11*). Thus the relative acidities for benzoic acid and benzoic acid-chromium tricarbonyl (XL) shown below suggest that the organo-metallic grouping iselectron with drawing in this instance.

Further evidence for the electron donating properties of the diene-$Fe(CO)_3$ group is seen in the following Friedel-Crafts reaction of 1-phenylbutadiene-iron tricarbonyl (XLI). The reaction proceeds under mild

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conditions to give a product identified as the *p*-acetyl compound (XLII).



The Electronic Structure of the Diene-Iron Tricarbonyl Complexes

As stated earlier it is now generally accepted that electronic interactions in many metallic complexes involve both "forward" coordination (donation of electrons from the ligand to the metal), and back donation (electrons from the metal to the antibonding orbital of the ligand). Thus the electron interaction involved in a metal-carbonyl bond of a metal carbonyl, may be schematically represented as in Figure 1. A similar situation is generally assumed to occur in the cases when olefins act as ligands.[1]

During the course of the present investigations several different types of diene-iron tricarbonyl complexes have been prepared in which the organic ligand possesses different electronic characteristics. The infra-red absorption spectra of these compounds have displayed regular variations, particularly of the CO stretching frequency, which are entirely consistent with a model based on the above types of orbital interactions. Insofar as our interpretation is correct, this model, which is discussed below, provides additional evidence for this type of bonding and supports the Hallam-Pauson structural formulation mentioned earlier.

Recent X-ray data (*12*) has shown that the disposition of the atoms in butadiene-iron tricarbonyl is as illustrated in Figure 2. If we assume that the atomic orbitals of iron involved in forward coordination of the diene are directed towards the center of the C=C bonds then it can be shown from group theory (*13*) that the best orbitals of Fe to use for this purpose are hybrids of $4s$, $4p^3$ and $3d_{xy}$ atomic orbitals. The molecular orbital involved in the forward coordination of each Fe-olefin bond will then be composed of the atomic orbitals shown in Figure 3 and occupied by the two electrons initially in the double bond.

For back coordination the same type of arguments suggest that the most important orbitals to consider are the antibonding molecular orbitals of the three carbonyl groups, the d_{xz} and d_{yz} orbitals of the iron atom, and the lowest unoccupied orbital of the conjugated diene. These interactions result in largely delocalized molecular orbitals and are schematically represented in Figure 4. It is this interaction which allows the high electron density in iron to be reduced, but it also weakens the carbon-oxygen bond. Now if the energy level of the antibonding molecular orbital were very high, this would be reflected in the resultant molecular orbital (Figure 4). Electrons in this latter orbital would tend to concentrate in the regions of the antibonding molecular orbital of the CO group thus weakening the CO bond energy. Conversely, if the diene antibonding orbital energies were very low, the CO bond would not be weakened to such an extent; and this would be reflected by their having an infrared absorption at higher frequencies than in the previous instance.

Another factor readily seen from Figure 4 is that for

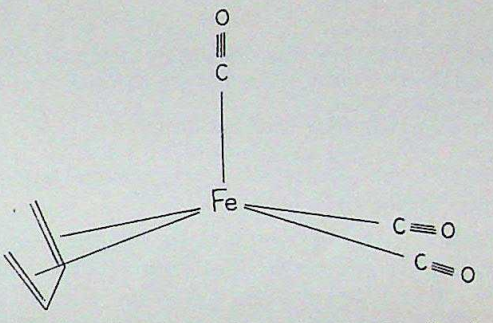


Figure 2. The disposition of atoms in butadiene-iron tricarbonyl.

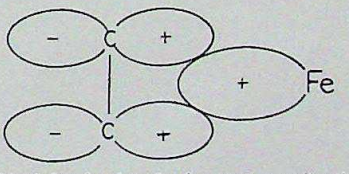


Figure 3. The orbitals involved in the forward coordination of an olefinic bond to iron in a diene-iron tricarbonyl complex.

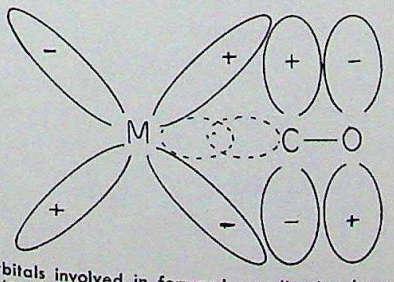


Figure 1. Orbitals involved in forward coordination (broken lines) and back donation (full lines) in a metal-carbonyl bond.

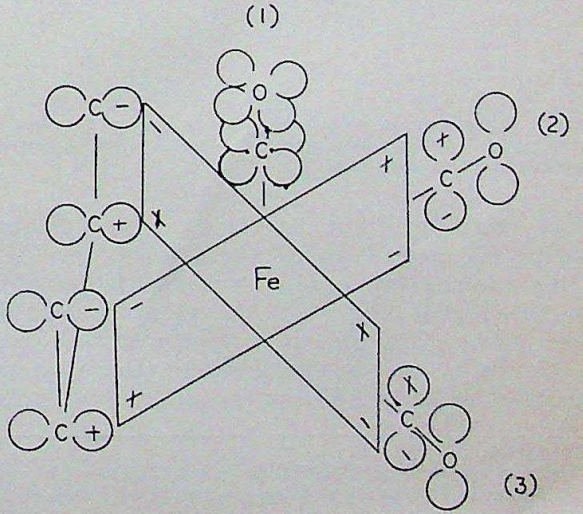


Figure 4. The orbitals involved in the back donation of electrons in a diene-iron tricarbonyl complex. For clarity the d orbitals of the central iron atoms are represented by two planes.

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complexes in which the two double bonds of the diene are not conjugated then, because of the orthogonality of the d_{xz} and d_{yz} atomic orbitals, two independent molecular orbitals will arise. The electron density distribution in these two will be determined by the same factors as discussed above. In particular, the carbonyl group (1) (see Figure 4) will be only influenced by that double bond which lies *trans* to it while CO(2) will be affected by the corresponding other double bond. The third carbonyl group will remain influenced by them both.

The series of diene-iron tricarbonyl compounds which have been prepared and whose infrared spectrum determined are listed in Table 1.[3] They are tabulated under various groups depending on the electronic nature of the diene. The infrared spectra invariably consist of two main regions of carbonyl adsorption, a narrow band and a broader band at slightly lower frequencies which is frequently itself split into two distinct peaks. The magnitude of the splitting of the broad band is given by δ.

The dienes are grouped according to their electronic properties in the following manner:

Group I—Butadiene.
Group II—Butadiene with a relatively inert substituent.
Group III—Butadiene with an attached strongly electron withdrawing substituent.
Group IV—Pentadienyl cationic ligands.
Group V—Non-conjugated dienes.
Group VI—Non-conjugated dienes possessing a strong electron withdrawing substituent.

Representative energy levels of the antibonding orbitals of the various groups, as determined by Hückel molecular orbital theory are given in Figure 5. The levels of the appropriate orbitals of Fe and CO are also included in this figure; although the relative positions of these are not known with any certainty this does not affect the qualitative argument.

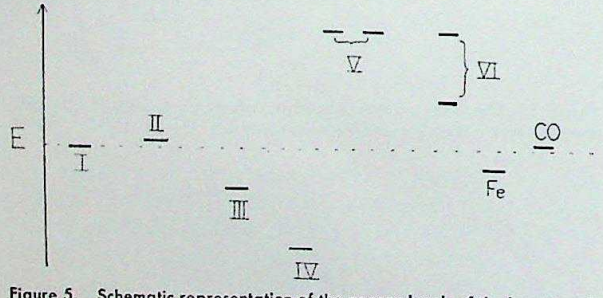


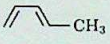
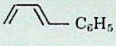
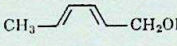
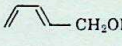
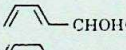
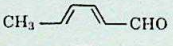
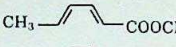
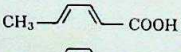
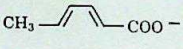
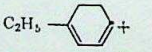
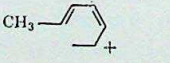
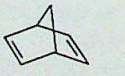
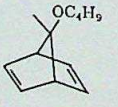
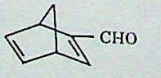
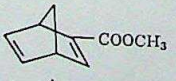
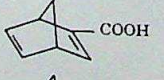
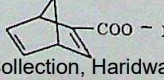
Figure 5. Schematic representation of the energy levels of the lowest antibonding orbitals of the various groups of dienes involved as ligands in diene-iron tricarbonyl complexes.

The more important aspects are briefly discussed below. The group II complexes show only small shifts in the carbonyl absorption compared to butadiene-iron tricarbonyl, in line with the relatively small electronic effects these substituents have on the orbital energies. For unsymmetrical dienes there is a small separation of the broad band explained on the basis of the electronic asymmetry being transmitted via the *d*-orbitals to the *trans* carbonyls.

The group III compounds show a definite shift to higher frequencies in accord with the lowering of the diene orbital energies due to the electron withdrawing substituent.

The group IV systems possess diene ligands having the lowest orbital energies of all and, in accord with this, the carbonyl adsorption is of highest frequency.

Table 1. Infrared absorption frequencies (cm^{-1}) of carbonyl group in various diene-$Fe(CO)_3$ complexes

Group	Diene ligand	Narrow band (cm^{-1})	Broad band (cm^{-1})	δ
I.		2057	1988	0
II.		2053	1987	0
		2049	1982 1974	8
		2050	1986 1979	7
		2049	1982 1975	7
		2054	1989 1978	11
		2053	1988 1977	11
		2048	1978	0
III.		2064	2002 1987	15
		2066	2000 1985	15
		2062	1996 1987	9
		2052	1987	0
IV.		2120	2072	0
		2110	2060	0
		2120	2072	0
		2120	2072	0
V.		2035	1967	0
		2033	1967	0
VI.		2050	1996 1975	21
		2049	1997 1971	26
		2051	1994 1969	25
		2038	1977 1959	18

[3] Several of these complexes were first reported by other authors, but in view of the emphasis we are placing here on relatively small spectral shifts, it was found desirable to repeat these preparations and record the infrared absorption data taken under the same conditions throughout the series.

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In contrast the group V members possessing non-conjugated diene ligands which have the highest orbital energies, show the lowest frequency of absorption.

Perhaps the most interesting effect is seen in the group VI complexes. The absorptions of these compounds are generally of low frequency in accord with the ethylene type ligands, but more significantly this group shows the largest values of δ, in complete accord with the large energy level separation of the antibonding orbitals of the diene shown in Figure 5.

One further comment concerns the two acidic complexes listed in Table 1. As would be anticipated from the model the absorptions of the corresponding anions occurs at lower frequency.[4]

The model used to explain the variations in the infrared spectrum is obviously a gross simplification of the actual system but it does seem to give results which are consistent with experiments for which no other explanation seems to be available.

[4] H. J. Dauben, Jr., and D. J. Bartelli, *J. Am. Chem. Soc.*, 83, 497 (1961) have also reported similar shifts in such compounds for anionic and cationic ligands.

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The Reaction of Tertiary Amines with Nitrous Acid

The study of the history of science has made it evident that the acceptance of new theories is a complicated process. Older notions which suggested that a particular experiment "overthrew" an established concept and immediately opened the way to a new one have been repeatedly challenged by careful examination of the historical record. It now appears that the overpowering influence of a critical experiment is often a romantic notion fostered in the act of eulogizing a particular scientist. The process of replacing an accredited theory with a new one has many steps. First, there is a period of rapid incorporation of facts within an old framework. Gradually, as the facts fail to fit neatly, an expansion and weakening of the framework occurs to accommodate new data. Next, or concurrently, may come a period where certain observations do not fit into the framework at all. They may be noted in a branch of the science far removed from theoretical work. After some time, new suggestions emerge, often limited to a few examples or with concessions to the older theory. Finally, a unifying concept develops such appeal that it can overcome all opposition and gradually replace the older concept. Perhaps one should add that all this is a continuing process, every "new" concept becomes an old established one after some time and is vigorously defended against attacks by skeptics.

It is not difficult to understand the reasons for resistance to change. The appreciation of a concept is a long process. Once an idea is learned, accepted, and used, it is difficult to discard it and accept a new one which may or may not be more useful. In discussing the origins of modern physics, Butterfield points out eloquently the difficulty of "putting on a new thinking cap (*1*)." Such revolutions in thinking do not occur often; it takes a remarkable man to be able to make the leap to a new concept.

A further appreciation of the inertia of the intellect can be attained by examining more humble examples of resistance to change. Not only new general concepts but even simple observations can have difficulty in becoming established if they are contrary to accepted notions. In these latter cases, the resistance is not based on the desire to retain a useful belief; rather, it involves intellectual laziness, an unwillingness to make the effort to incorporate an unrelated fact into a crowded network of ideas. Contrary to popular belief, many scientists, like many people generally, suffer from a conservatism which causes them to resist conceptual changes.

Most people try to simplify life. One way to do this is to recognize only part of the multitude of sensations which impinge upon us. Such selectivity is necessary to order the universe. However, when applied to the

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conduct of an experiment, it often happens that the investigator observes only the phenomena which have a direct relation to what he wants to discover. Probably most scientists are more likely to repeat an experiment which goes "wrong" rather than one which goes "right." It is important to remember that these evaluative terms only have meaning within the framework of the particular scientist's knowledge, background, and interests.

Early History

The conservatism which prevents scientists from recognizing as significant those experiments which are contrary to accepted beliefs is illustrated by the history of the reaction of tertiary amines with nitrous acid. This reaction is a well established phenomenon. It has been discussed vigorously in texts and papers since 1864; it has been independently "discovered" at least three times as a general reaction; and there are many separate examples reported in the literature. Yet, the reaction is mentioned less often in each succeeding generation of texts:

In 1866 Heintz published a definitive paper (*2*) demonstrating that tertiary amines do *not* react with nitrous acid. He did this mainly to refute a paper by Guether (*3*) published two years earlier, in which it was reported that triethylamine gave some *N*-nitrosodiethylamine when treated with nitrous acid. Heintz found no evidence for this reaction and suggested that perhaps Guether's triethylamine was contaminated with some secondary amine. At that time the separation of the alkylation products of ammonia was difficult and his explanation is reasonable. Also his own experiments are sound and comprehensive. There is no reason to doubt his results. The now well known "inertness" (except for salt formation) of tertiary amines towards nitrous acid and the use of this reagent to separate classes of amines has been discussed as the "Heintz method" (*4*).

Yet, only one year later, Limpricht (*5*) reported that nitrous acid did react with tribenzylamine in a complicated manner. No matter how he attempted to control conditions, the reaction took a variable course. Limpricht did succeed in partially identifying some reaction products. First, he noted that one product of the reaction was often benzaldehyde. He demonstrated that this was probably a primary product, rather than a biproduct derived from the oxidation of some primary benzylic compound, such as benzyl alcohol, under the reaction conditions. Secondly, in one attempt, he isolated a low melting solid from an oil which had collected above the reaction mixture. Although he failed to identify the solid, it was probably *N*-nitrosodibenzylamine (*6*). Limpricht does not mention Heintz' paper, but he has taken precautions to be sure that his tribenzylamine was pure, uncontaminated by secondary amine. On the whole the two papers are comparable. Each is the result of careful work; starting materials are purified and experiments described in detail. Heintz comes out with a neater argument, but then he is reporting negative results. Limpricht cannot pin down the phenomenon he observes, but he did identify the major reaction products.

Although nitrous acid became a tool for separating secondary and tertiary amines, it was more or less accepted that tertiary amines also reacted with this reagent. Influential texts, such as Meyer-Jacobson, (*7*) mentioned the reaction, and in 1896 Kishner (*8*) reported the preparation of *N*-nitroso-*N*-ethylmenthylamine from *N*,*N*-diethylmenthylamine and nitrous acid in weakly acid solution. He wrote equation (1) for the reaction.

$$C_{10}H_{19}N(C_2H_5)_2 + HNO_2 \rightarrow C_{10}H_{19}N(C_2H_5)NO + C_2H_5OH \quad (1)$$

He commented, without reference, that "like most aliphatic tertiary amines, diethylmenthylamine loses one of its radicals as an alcohol by the action of nitrous acid." Some years earlier, E. Schmidt (*9*) had attempted to purify trimethylamine by heating the crude compound with nitrous acid. He found to his disappointment, that the product was less pure than the starting material!

Rediscovery in 1920

Despite these reports, some of which are listed in Beilstein, the reaction essentially disappeared from the chemical literature. It became so neglected that it was "discovered" in 1920 and patented by chemists at Merck and Co. (*10*). They were interested in methods of preparing *N*-nitroso compounds and were delighted to note that not only secondary amines but even tertiary ones could be converted into the desired products despite the fact that "not only in all the texts, but even in colleges, one is taught that tertiary aliphatic amines do not react with nitrous acid."

This patent received proper circulation and resulted in two general papers on the reaction. Degradative procedures for tertiary amines are of particular interest in alkaloid chemistry. Speyer and Walther (*11*), on the basis of the patent, suggested that this reaction might replace the von Braun degradation which involves the reaction of cyanogen bromide with tertiary amines. They did not suggest a mechanistic analogy but a formal one.

$$R_2NR' + BrCN = R_2N{-}CN + BrR' \quad (2)$$

$$R_2NR' + HONO = R_2N{-}NO + (HOR') \quad (3)$$

They tried six examples chosen from the morphine alkaloids and, except for morphine itself, which is readily oxidized to a dimer by mild oxidizing agents, they succeeded in degrading morphine and codeine derivatives to *N*-nitroso products of the *nor* series. Almost simultaneously the method was used by Ochiai (*12*). These papers were the origin of a limited tradition of nitrosative degradation of alkaloids. Since then Abubakirov and Yunosov (*13*) and Cookson and Trevitt (*14*) have used it for certain lupine alkaloids. Probably the same reaction is involved in Craig's degradation of related compounds by nitrous and nitric acids (*15*), and in Goodson and Henry's nitrosation of echitamine (*16*). The latter reaction could not be repeated by Chatterjee (*17*), who may have worked with more acid solutions.

The set of papers just mentioned represents a sample from one branch of organic chemistry. The scope of organic chemistry is so great that workers in one research area may use reactions which are not generally known and which are not well understood. Thus, the

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references in the papers on alkaloid chemistry may refer to previous work in the same area; it is implied that this degradation is characteristic for alkaloids, not for tertiary amines generally.

In a similar manner, the evidence from one field of natural products research does not seem to have been noted by other chemists. In 1936 Wegler and Frank (*18*) published a definitive paper on the reaction, really the first except for Limpricht's contribution. Wegler and Frank came upon the reaction accidentally while trying to purify isobornylamine. Like many others before them, they encountered difficulty with the nitrous acid procedure. Perhaps it was the readily detectable camphor, one of the products, which led them on. In any case, they recognized what was going on and made a successful generalization. First, they attempted to survey the literature of this reaction. Although rather incomplete, their bibliography did give some telling examples including the Merck patent. Secondly, they tried to rationalize the reaction. Without going into details, they pointed out the similarity to the von Braun reaction and to other degradative procedures for tertiary amines. Thirdly, they converted approximately a dozen tertiary amines into *N*-nitroso secondary amines and aldehydes or ketones. Yields of carbonyl compounds were 30 to 60% plus some recovery of starting materials. Finally, they apparently defined the proper reaction condition: most reactions were run at 40° to 80° in acetic acid. Unfortunately, in the next year the same authors published a rather disappointing note (*19*) on attempts to use the reaction for some particular synthetic problems. For unknown reasons they had switched to a mixture of NO_2 and O_2 in acid as the nitrosating agent and reported poor yields of products and increased occurrence of side reactions.

Other Work

Several other instances of the reaction of tertiary amines with nitrosating agents have been reported. T. H. Reade and collaborators published a series of papers (*20*) on the reactions of substituted dialkyl anilines. They showed conclusively that at least some of the products must arise from nitrosatine cleavage of the tertiary amine and they demonstrated the nature of the organic products as indicated in reaction (4).

$$p\text{-P}—C_6H_4N(CH_3)_2 + HNO_2 \rightarrow p\text{-R}—C_6H_4N(CH_3)NO + CH_2O \quad (4)$$

The reaction is particularly successful along this path if the readily nitrosated para position of the ring is blocked.

Reade seems to have been unaware of the related work on aliphatic amines. He believed that this reaction was peculiar to aniline derivatives. Although this work was based on earlier observations (*21*), is discussed in modern publications (*22*), and has been suggested as a preparative method for nuclear substituted monoalkylated anilines (*23*), no organic text in common use mentions the reaction. All of them point out that aromatic tertiary amines, in contrast to aliphatic ones, do react with nitrous acid but only to give nuclear substitution products.

Other nitrosating agents can also bring about this reaction. Calvert and Calvert (*24*) reported the formation of the *p*-nitroso-*N*-methyl-*N*-nitrosoaniline on treatment of *N*,*N*-dimethylaniline with a compound obtained by the action of nitrous acid on benzyl alcohol. Their unknown compound may have been benzyl nitrite. More to the point, Sitka and Rolfes (*25*) obtained *N*-nitroso-*N*-methylcyclohexylamine on treatment of *N*,*N*-dimethylcyclohexylamine with nitrosyl chloride at zero degrees in dry ether. They did not isolate any other product but reported that the reaction mixture had an odor of formaldehyde. Finally, the reaction of hexamethylenetetramine with nitrous acid yields products indicative of the same type of reaction (*26*).

Recent Observations

The last two decades have resulted in few examples of the successful nitrosation of tertiary amines. Some of the older textbooks, popular before World War II, mention the reaction very briefly, but the newest ones shun it with only one exception. It was not surprising that the reaction was again "discovered." The characteristic cleavage was first observed by Pars (*27*) during attempted nitrosations of substituted hydrazines, and then the general nature of the reaction was elucidated by Smith and Pars (*28*).

With a modern appreciation of reaction mechanisms it was possible to develop a reasonable explanation for the reaction path as well as to indicate why the reaction could have had such a checkered career. Smith and Pars (*28*) propose that the nitrosation of tertiary amines involves electrophilic attack on amine nitrogen followed by 1,2 elimination to give an imminium compound which is hydrolyzed to the final products.

$$R_2CH—\ddot{N}R_2' + NO^+ \rightarrow R_2CH-\overset{+}{N}(R_2)NO \rightarrow R_2C{=}NR_2'^{+} + HNO$$

The *N*-nitroso derivative of the secondary amine, the observed reaction product, would result from nitrosation of the secondary amine after hydrolysis of the imminium intermediate. This path is analogous to several other reactions of amines: the action of bromine on tertiary amines as well as the degradation of amine oxides in acid or by means of sulfur dioxide can be similarly formulated (*28*). The other nitrogenous product, nitroxyl, HNO, is known as an elimination product from a number of similar organic reactions where C-NO or N-NO bonds are broken (*29*).

Like most electrophilic attacks on amino nitrogen, the reaction is *p*H dependent. The free amine is reactive, the ammonium salt is, at best, many powers of ten less reactive. Thus, when nitrous acid was brought in contact with tertiary amines in fairly concentrated acid solutions (*p*H less than 3), no reaction was observed in cold dilute solutions. However, at higher *p*H ranges (*p*H 3 to 6), especially at elevated temperatures or in concentrated nitrite solutions, the nitrosative decomposition can be observed. From the recorded examples it is clear that all the "successful" work was performed under one or more of the latter conditions. Guether (*3*) carefully neutralized both amine salt and nitrite solutions, Kishner (*8*) stresses that the reaction takes place in weak acid, and others had worked with excess nitrite ion.

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Mechanism

The first balanced equation for this reaction was the one written by Kishner (*8*) (see equation 1 above). This was adopted by Karrer in his text (*30*), although aldehydes have often been reported as products and there is no evidence that alcohols are ever formed. Perhaps this equation was favored because it permits a simple stoichiometric relationship. Any mechanism involving an oxidation of an alkyl residue as an integral part of the reaction requires more complicated stoichiometry and raises a question concerning the fate of the nitrogen species which causes the oxidation.

At present the detailed path is being investigated (*31*). There is every reason to believe that the path for nitrosation of tertiary amines is, at least in the initial stages, similar to the reaction path for primary or secondary amines with the same reagent. In each case it is assumed that the unprotonated amine reacts, using the unshared electron pair, with an electron deficient nitrogen bearing species

$$R_3N: + NO^+ \rightarrow [R_3N{-}NO]^+$$

The intermediate first formed then stabilizes itself in some way, usually involving loss of a proton if one or more R groups is equal to hydrogen.

$$R_2NH{-}NO^+ \rightarrow R_2N{-}NO + H^+ \text{ (nitrosamine)}$$

$$RNH_2{}^+{-}NO - H^+ \rightarrow [RNH{-}NO] \rightarrow [RN{=}NOH] \rightarrow [RN_2{}^+] \rightarrow \text{etc.}$$

The significance of the similarity of mechanism for these three classes of amines is that the unprotonated nucleophilic amine is considered to be the active reagent and that the intial step involves an addition to the amine of an electrophilic reagent.

Several texts not only ignore the reaction of tertiary amines with nitrous acid; they go further and suggest reasons why the reaction fails. They claim that the reaction fails with tertiary amines because these have no hydrogen which can be displaced by the nitrosating agent. Statements like the above imply a concerted mechanism involving electrophilic displacement on nitrogen, a rather unlikely prospect in acidic solutions.

Conclusions

The suggested explanations for the inertness of tertiary amines towards nitrous acid represent the final step in the failure of this reaction to be accepted in the general literature. Somehow, the recorded observations have never penetrated the maze of generally accepted information although the reaction should be expected in the light of current mechanistic considerations. True, the reaction proceeds only under limited conditions, but so do most processes.

It is interesting to speculate on the tenacity of the mistaken belief in the face of the mechanistic knowledge which predicts that the reaction should be observed. Here is a case where the new knowledge still has to force out an old belief long after the utility of the old concept has vanished and long after the facts have made it untenable.

No doubt the lack of recognition of this reaction has prevented its full use from being developed. As has been suggested previously, the decomposition of alkaloids by means of nitrous acid ought to be a useful reaction. The conditions are much milder than most other such degradative schemes. The very limited use probably results in part because of lack of knowledge concerning the proper experimental conditions. By use of acetate buffers the reaction can be carried out under rather mild conditions. Only recently has any attempt been made (*31*) to extend some qualitative observations by Wegler and Frank (*18*) that the ease of splitting of alkyl groups is benzyl > alkyl > cyclic. It is time that a reaction with so much supporting evidence be recognized generally so that it need not be "discovered" again in another decade!

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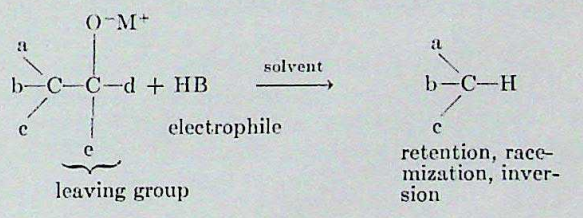
Multicenter and Assisted Mechanistic Pathways in the Reactions of Organometallic Compounds

Raymond E. Dessy[1]
and **Frank Paulik**
University of Cincinnati
Cincinnati, Ohio

If one examines the possible mechanistic pathways that substitution at an attacked saturated center may take, two main divisions may be easily listed without consideration of fine detail: (1) nucleophilic, S_N, and (2) electrophilic, S_E, processes. These are illustrated below, with X-Y the substrate, and E-N the attacking reagent in molecular form. The notations employed are the basic Ingold classification scheme (*1*). In the same manner, simple addition processes may be divided into similar categories. (Table 1, 2)

The S_N series involving saturated carbon centers has been the subject of a great deal of work, and though some minor disagreements still exist concerning intimate details, particularly solvent participation, our over-all picture of the area is relatively clear. S_N2 reactions usually yield product with inverted configuration, S_N1 processes may proceed with racemization, predominant inversion, or predominant retention of configuration, while S_Ni processes give a prior retention of configuration. (The work of Sommer has shown that at saturated silicon centers S_N2 processes may proceed with retention of configuration (*2*), presumably because of *d* orbital participation allowing front-side attack by the nucleophile.)

S_E processes are less completely understood, fundamentally because the generation of an incipient or free carbanion in the rate determining process implies the use of organometallic compounds, most of which are labile to water and/or oxygen, necessitating vacuum-line or inert atmosphere box techniques. Only one isolated case of an S_E1 reaction in an organometallic system (organomercurial) has been reported (*3*), and no detailed stereochemical or mechanistic investigation was undertaken. However, from the excellent work of Cram (*4*) on the system indicated below it is known



[1] Alfred P. Sloan Fellow; Texaco, Inc., Predoctoral Fellow.

Table 1.

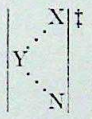
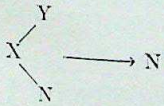
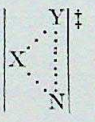
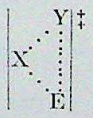
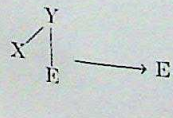
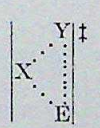
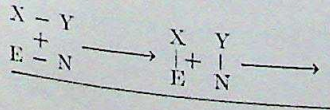
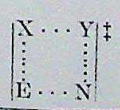
Reaction	Transition state	Classification
$X-Y+N: \rightarrow N-Y+X:$	$\lvert N\cdots Y\cdots X\rvert ‡$	S_N2
or		
$X-Y \xrightarrow{slow} X: + Y$		S_N
$Y+N: \xrightarrow{fast} N-Y$	$\lvert X\cdots Y\rvert ‡$	S_N1
		S_Ni
$X-Y+E \rightarrow C-X+Y$	$\lvert E\cdots X\cdots Y\rvert ‡$	S_E2
or		
$X-Y \xrightarrow{slow} X: + Y$		S_E
$X: + E \longrightarrow E-X$	$\lvert X\cdots Y\rvert ‡$	S_E1
		S_Ei
		S_F

Table 2.

Reaction	Transition state	Classification
$X=Y+N: \xrightarrow{slow} :X-Y$ (N)	$\lvert X{=}Y\rvert ‡$ (N)	Ad_N
$:X-Y+E \longrightarrow X-Y$ (N; E, N)		Ad_N
$X=Y+E \xrightarrow{slow} X-Y$ (E)	$\lvert X{=}Y\rvert ‡$ (E)	Ad_E
$X-Y+N \longrightarrow X-Y$ (E; E, N)		Ad_E
$X=Y+E-N \longrightarrow X-Y$ (E, N)	$\lvert X{-}Y\rvert ‡$ (E, N)	Ad_F

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that the possible stereochemical consequences of S_E1 reactions are similar to those of S_NI reactions (Fig. 1). Factors contributing to the specific courses taken by any one reaction have been discussed by Cram (*4*), Streitwieser (*5*), Corey (*6*), and Goering (*7*), with particular emphasis on those reactions involving H/D exchange at an optically active center *via* carbanion (ion-pair) intermediates. The temperature, solvent, availability of internal proton, and cation of the base are all apparently important.

Three distinct types of optically active centers have been employed. Cram has investigated hydrogen exchanges α to a nitrile, amide, or ester function. Streitwieser, and Cram have investigated benzylic hydrogen exchanges, while Corey, Goering, and Cram have studied the exchange reactions of hydrogens α to an activating sulfone grouping. The first case is of little interest here since exchange seems to involve an ambident anion capable of protonating on the most electronegative element to give an unstable tautomer which reverts to exchange product with *a priori* racemization (Fig. 2). The latter two cases are interesting in the sense that some light is shed on the relationships between the factors mentioned above, as well as the effect of the structure of the carbanion.

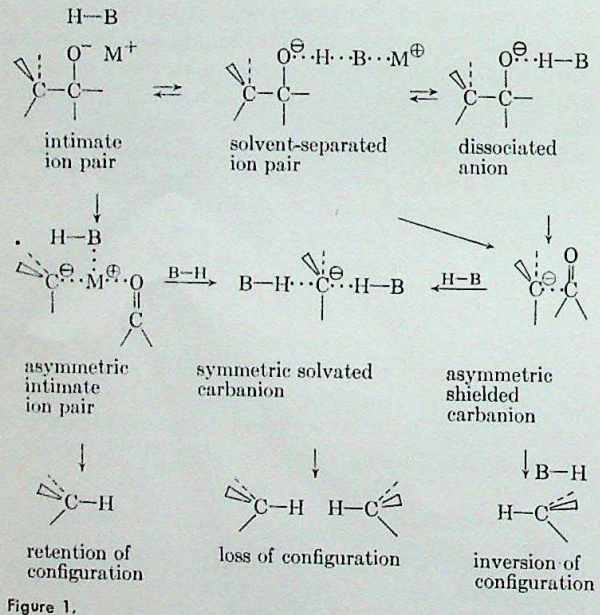


Figure 1.

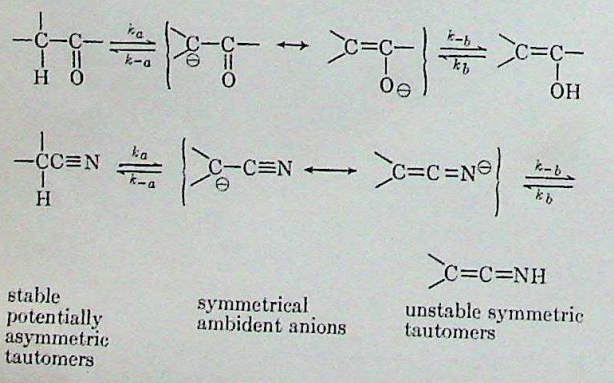
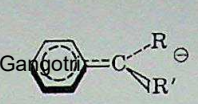
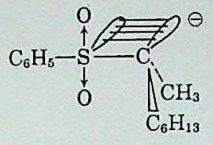


Figure 2.



benzylic carbanion

Sulfone carbanions appear to be asymmetric because of stabilization by the adjacent SO_2 function, through overlap of the carbanion $(sp^3)^2$ orbital and empty sulfur *d* orbitals, while benzylic carbanions would appear



sulfone carbanion

to be predominantly symmetrical because of delocalization of the charge into the ring. Yet, both types of carbanions are capable of exhibiting exchange processes that are predominantly racemizing, or retentive in nature (Table 3). It would seem essential to invoke some type of solvent participation to explain the results obtained. The concepts of Cram regarding the intimate solvation pictures which lead to retention and racemization (or inversion) are charted in Figure 3. At present there is no clear agreement concerning the exact nature of the solvent interactions leading to retention: Cram feels that "...the active catalytic species are heavily solvated metal-alkoxide ion pairs and the carbanion-metal cation pair produced is heavily solvated on the front side with deuterium donors because of the solvent orienting powers of the metal cation. Thus deuterium capture from the front side is the favored reaction path." Streitwieser, on the other hand, feels that front-side attack predominates because reaction at the rear produces charge separation in a media of poor ionizing power. If he can "formulate this distinction in operational terms that may be subject to experimental test," our exact knowledge in this important area will be greatly improved.

Table 3. Carbanion-Solvent-Base Systems Classified According to Their Symmetry Properties

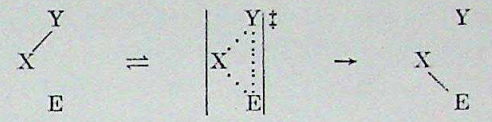
Class	Carbanion	Solvent shell	Examples
I	Symmetric	Symmetric	2-Phenyl-2-butyl anion in either dimethyl sulfoxide–potassium *t*-butoxide, or *t*-butyl alcohol–quaternary ammonium hydroxide
II	Symmetric	Asymmetric	2-Phenyl-2-butyl anion in either *t*-butyl alcohol–potassium *t*-butoxide, or ethylene glycol–potassium ethylene glycoside
III	Asymmetric	Symmetric	2-Phenylsulfonyl-2-octyl anion in dimethyl sulfoxide–potassium methoxide, or in *t*-butyl alcohol–tetramethylammonium hydroxide
IV	Asymmetric	Asymmetric	2-Phenylsulfonyl-2-octyl anion in *t*-butyl alcohol–potassium *t*-butoxide

The detailed aspects of S_E2 reactions have been most clearly discussed by Winstein (*8, 9*) and more recently by Charman, *et al.* (*10*).

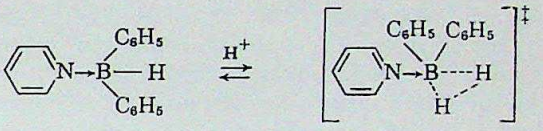
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Winstein concluded that, a priori, it is difficult to predict whether front-side attack (retention) or back side attack (inversion) will be the normal mode of substitution by this mechanistic pathway. The dichotomy arises from the fact that in S_E2 transition states it is not necessary for carbon to "expand its octet" as in S_N2 processes. The electronic repulsions between incoming and departing groups, which in S_N2 reactions give rise to the drastic differences in activation energies for front-side versus back-side attack, are not important in S_E processes. Winstein has pointed out that 3-center bonding may indeed favor front-side attack as compared to back-side attack in such reactions.



At least one case involving a three-center transition state has been reported. Hawthorne (*11*) has, on the basis of deuterium isotope studies, claimed that the acid cleavage of a b—H bond is a three-center process.[2]



Sufficient data to settle the dichotomy is not yet available. Two series of reactions which might be labeled S_E2 processes have been investigated.

$$R_2Hg + HgX_2 \rightarrow 2RHgX$$

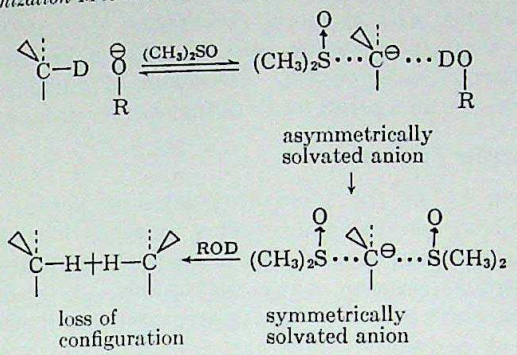
$$R_2Hg + HX \rightarrow RH + RHgX$$

The relative sequence of reactivities found for various R groups in the above reactions, or related reactions, are listed in Table 4.

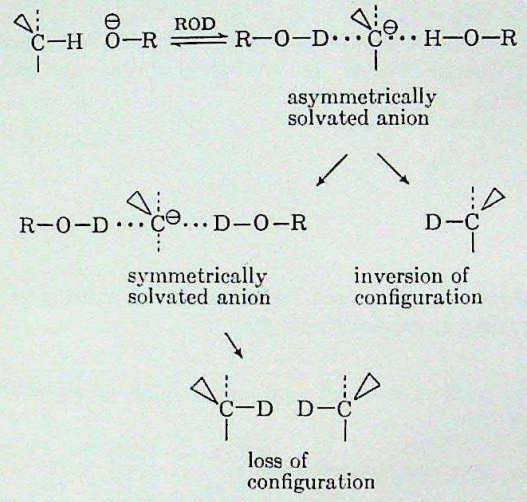
Two reaction types seem indicated by a casual observation of this data.

Charman, Hughes, and Ingold (HgX_2/EtOH) have suggested that they were observing an S_E2 reaction. Use of optically active R groups (*sec*-butyl, 4-methyl-

Racemization Mechanism:



Inversion Mechanism:



Retention Mechanism:

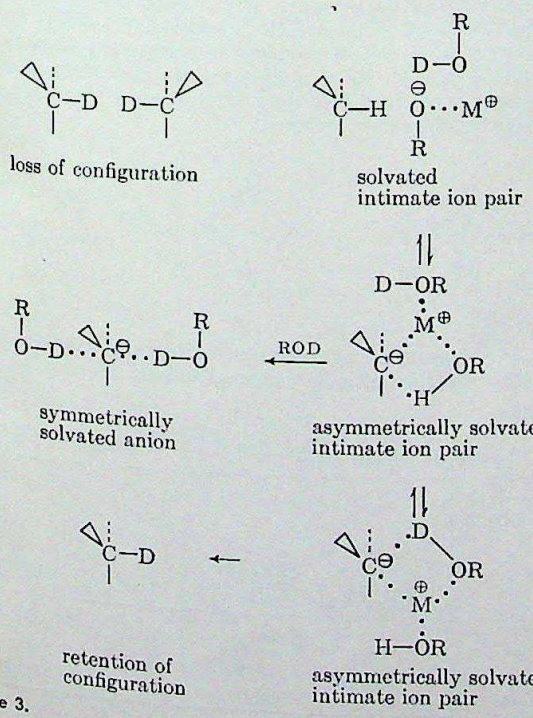
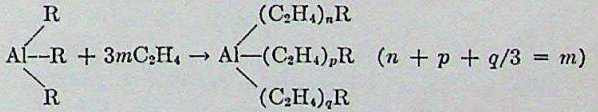


Figure 3.

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[2] The symbolism *m* is used to represent a metal and *one* of its valencies—it is a useful notation that avoids having to portray the rest of the organometallic compound, which is often very complicated, and perhaps the structure of which is unknown. It replaces the older symbolism $(1/n)M$, where n is the valence of the metal. For example in the Ziegler type olefin, aluminum alkyl reactions



$$(n + p + q/3 = m)$$

are obviously more easily written and understood as

$$RAl + mC_2H_4 \rightarrow R(C_2H_4)_mAl$$

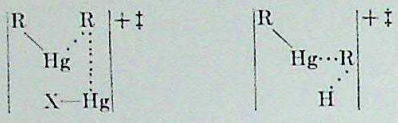
An excellent example of the use of this symbolism is found in the chapter by K. Ziegler in Zeiss, H., "Organometallic Chemistry," ACS Monograph No. 147. It is of obvious advantage in dealing with the reactions of Grignard reagents, where the exact structure is unknown in ether; thus R-mg, not RMgX which is incorrect, or $R_2Mg \cdot MgX_2$ which is awkward, or "RMgX" which is perhaps the only reasonable alternative. It also focuses on a particular bond when a series of related, but different compounds are employed, i.e., $RSnR_3$, $R\text{-}SnR_2Cl$, $R\text{-}SnRCl_2$, etc., may be represented as R-sn.

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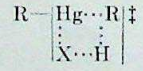
cyclohexyl, and isoheptyl) by three different groups—Jensen (*12*) in California, Charman, *et al.* (*13*) in England, and Reutov (*14*) in Russia had shown that retention of configuration is observed under a variety of experimental conditions for similar reactions.

Transition states of the following type seem appropriate for the reactions reported by Charman, Kreevoy ($HClO_4$/HOAc), and possibly for some of Jensen's reactions, the conclusion being that S_E2 processes involving the cleavage of a carbon-mercury bond proceed by front-side attack, and retention of configuration. It is not possible to extrapolate



these findings in the process of electrophilic substitution at a saturated carbon center, without restriction, to the cleavage of other carbon-metal bonds. (Brown (*15*) has shown, that in a constrained ring system the cleavage of carbon-boron bonds proceeds with retention, but the mechanism of the reaction is unclear, and may involve concepts similar to those which follow.)

This still leaves unexplained the different sequence of reactivities found for cleavage of carbon-mercury bonds in dimethylsulfoxide/dioxane by HX, and in dioxane by HgX_2 compared to the sequence found in $HClO_4$/HOAc and HgX_2/EtOH cleavages, and the fact that Jensen reports that non-polar solvents and halogen acids enhance the stereospecificity of the acid cleavages. Dessy (*16*) has interpreted the kinetic findings associated with the first reaction, under these conditions, as involving a four-center transition state, e.g.,



The transition state for HgX_2/dioxane cleavages appears to be four-center in character also, but there is uncertainty about its exact nature.[3]

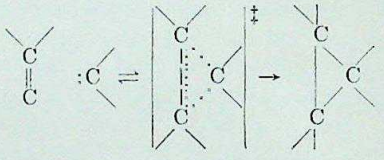
The conclusion would be that the change in solvents resulted in a change of mechanism. Although stereochemical and kinetic studies on the same system in a variety of solvents in the mercury system have not been undertaken, some work by Gielen (*18*) suggests that this interpretation is correct. Summarized in Table 5 is the relative sequence of reactivities for the cleavage of R—sn bonds[2] by a variety of reagents, under a variety of conditions.

Gielen has pointed out that there is an obvious correlation between these observations in the tin series, and those previously indicated for cleavage of carbon-mercury bonds. Two separate sequences of reactivity as a function of R exist in both systems, and aprotic and aprotic-polar environments lead to one (CH_3 < R), while protic environments lead to the other ($CH_3 > C_2H_5 > C_3H_7 > i\text{—}C_3H_7$). Presumably the latter is due to a mechanism of the type S_E2, while the former is the result of a four-center process. In the mercury case it seems established then that the stereochemical consequences of S_E2 processes are retention of configuration. Retention of configuration is, of course, an a priori result of four-center processes.

Multicenter Processes

A survey of the literature makes it appear that multicenter processes are being suggested with an increasing frequency to explain experimental results. An *n*-center reaction is one that involves a transition state in which bonding changes are occurring simultaneously at *n* different sites arranged in a ring system. The following are some examples of such multi-center reactions.

Three-center processes have been postulated, notably in carbene insertions (*19*) and in acid cleavage of b—H bonds[2] as

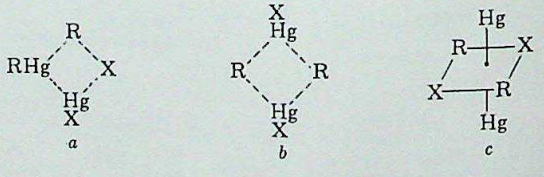


mentioned earlier but little more is known of this potentially important pathway.

[3] The problem involved may best be summed up by viewing the reaction

$$\text{RHgR}' + \text{Hg*X}_2 \rightarrow \begin{matrix}\text{RHgX} + \text{R}'\text{Hg*X} & \text{I}\\ \text{RHg*X} + \text{R}'\text{Hg*X} & \text{II}\\ \text{RHg*X} + \text{R}'\text{HgX} & \text{III}\end{matrix}$$

Winstein (*39*) (R = neophyl, R′ = cis-2-methoxycyclohexyl) and Dessy (*16*) (R = phenyl, R′ = ethyl) find case II: Broderson (*40*) (R = phenyl, R′ = butyl) reports case I, while Reutov (*41*) (R = phenyl, R′ = ethyl) reports case III. Until this trichotomy is resolved it is not known whether transition states *a* and/or *b* and/or *c* are involved:



Extensive investigations under a variety of conditions will probably reveal a multiplicity of mechanisms.

Table 4. Relative Reactivities for Rhg + E—N → RE + HgN

R \ E—N, solvent	HgI_2[a] / dioxane	HCl[b] / DMSO-dioxane	$HClO_4$[c] / HOAc	HgX_2[d] / EtOH
CH_3	Too slow to measure	1	1	1
C_2H_5	1.63	6.3	0.65	0.42
C_3H_7	1.86	3.9	0.36	...
$i\text{-}C_3H_7$	1.60	4.3	...	...

[a] Ref. (*16a*); [b] Ref. (*16b*); [c] Ref. (*17*); [d] Ref. (*16a*).

Table 5. $R_4Sn + E\text{—}N \xrightarrow{\text{solvent}} R_3SnN + RE$

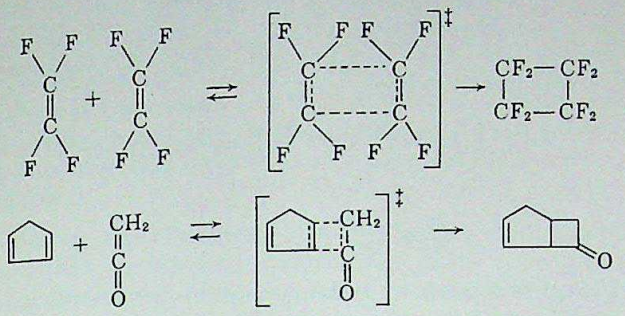
R \ E—N solvent	I_2[a] / C_6H_5Cl	HCl[b] / C_6H_6	I_2[c] / MeOH	I_2[d] / HOAc
CH_3	1	1	1	1
C_2H_5	11.5	8.8	0.12	0.37
C_3H_7	4.5	3.8	0.01	0.04
$i\text{-}C_3H_7$	13.5	3.7	...	0.0004

[a] Ref. (*18*); [b] Ref. (*19*); [c] Ref. (*48*); [d] Ref. (*49*).

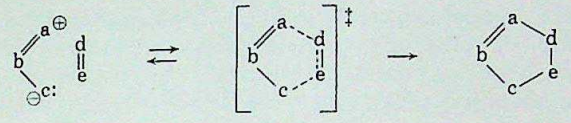
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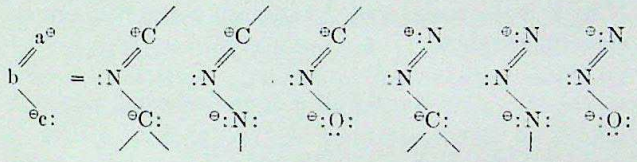
Four-center reactions in normal carbon chemistry are rare. The dimerization of tetrafluoroethylene or the reaction of ketene and cyclopentadiene appear to be four-center in nature (*19*)



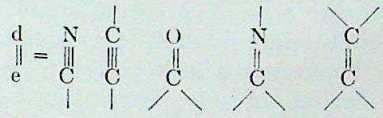
Five-center transition states have been brought to the fore-front recently by the excellent work of Huisgen (*20*) on 1, 3 dipolar additions.



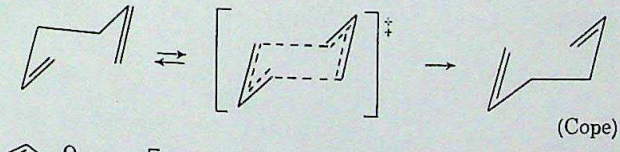
where for example



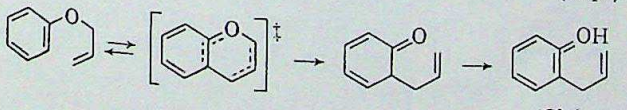
and



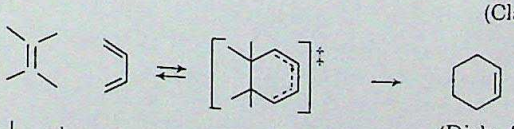
Six-center reactions are, of course, quite familiar. For example one might cite the Cope, Claisen, Diels-Alder and Chugaev reactions, and the pyrolysis of esters



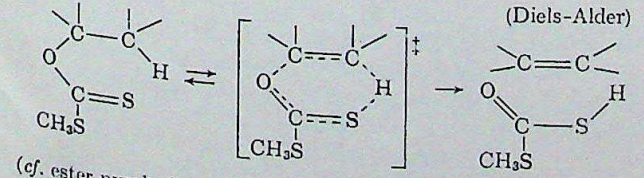
(Cope)



(Claisen)



(Diels-Alder)



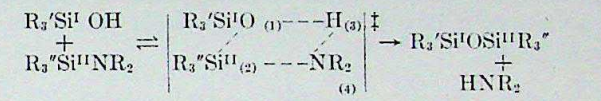
(*cf.* ester pyrolysis)

(Chugaev)

Kinetic and mechanistic data adequately substantiating multicenter mechanisms are hard to obtain. Stereochemistry and the expected lack of solvent effects on these non-ionic mechanisms are the most persuasive tools. Despite these difficulties the four-center mechanism appears with regularity in discussions of organometallic reaction mechanisms for reasons which will be discussed.[4]

The Four-Center Mechanism

Since a four-center transition state may be defined as a condition in which bonding changes are simultaneously occurring at four different atoms in an activated transition state complex, it then follows that in a multicenter transition state the rate and course of reaction should be dependent upon the bonding properties of all attacked and attacking sites. Broadly speaking, such "properties" would be reflected in the electron donating and electron accepting properties of these sites. This being so, it should be possible to change the bonding characteristics of any one or all of these sites by varying the groups initially attached to them, and then to observe the effects of these changes on the reaction rate. This is illustrated by the reaction of silanols with silylamines (*21*).



Varying the groups on the silanol would not only affect its ability to coordinate with the silylamine (sites 1 and 2), but would also affect its acidity and therefore the proton transfer to the nitrogen atom (sites 3 and 4). The kinetic data obtained indicates that when the same silylamine is used, the reaction rate increases with the acidity of the silanol, $(C_6H_5)_3SiOH > Et_3SiOH$. It appears then that the coordinating properties of the silanol are not as important as its acidity; however, it is important to note that such coordination by the silanol also reinforces its acidity. The change of the acidity or other physical and chemical properties of a ligand upon coordination has long been an area of interest in inorganic chemistry.

When the groups around the nitrogen atom in the silylamine are varied, the basicity of the nitrogen atom and its ability to bond to the proton are also changed (sites 3 and 4). Thus +I groups will increase basicity and −I groups will decrease basicity. Examining the kinetic data, we find that the more basic silylamines, R″ being constant, react more rapidly and *N*,*N*-dialkyl > *N*-alkyl. Finally, varying the groups around silicon, site 2, would alter its ability to coordinate with the silanol, −I groups facilitating this interaction and +I groups retarding it. Thus, when the amine

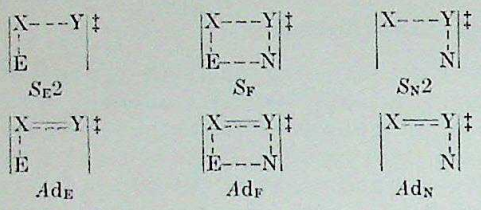
[4] The authors have prepared an annotated bibliography of these four-center mechanisms. They either have been proposed by the original investigator, or sufficient data are available to suggest a four-center reaction. Organometallic compounds involving Li, Be, Mg (6 cases), B (10 cases), Hg (6 cases), Zn, Cd, Tl, Si and Sn (7 cases) are represented. The list is by no means complete since mechanisms are not abstracted. Copies of the bibliography are available from the authors upon request. The authors would appreciate correspondence with interested readers who may be able to call attention to reactions otherwise not noted.

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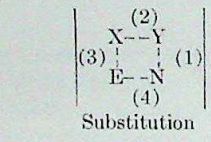
residue is held constant, the more electronegative silicon, which coordinates more strongly with the silanol, is more reactive and the order of reactivity was found to be $(CH_3)_3Si > (Et)_3Si > (n\text{-}Bu)_3Si$. (Steric factors may be present here also.)

Conceptually then, one can visualize the transition state for a concerted four-center process (Table 1, 2) as intermediate between the limits S_N2, S_E2, or Ad_N, Ad_E.



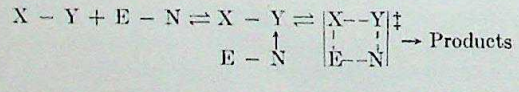
Although such totally concerted processes would be disfavored by entropy considerations, in most cases they would be favored by enthalpy considerations, since they do not require that as high a charge be placed on the atom(s) undergoing bonding changes as the potential barrier is crossed.

In a further consideration of the four-center substitution mechanism, it is very meaningful to ask searching questions about the timing involved. If we label the various bond making/breaking processes as indicated below it seems reasonable to expect, as mentioned



Substitution

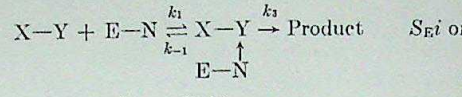
before, that a totally concerted process (1,2,3,4) will be unfavorable, entropy-wise, and it is possible that lower energy routes are available. In organometallic compounds, R—M (X = R, Y = M), where M possesses an incomplete octet, or can expand its octet, a pre-rate determining complexing of the type $E - N \rightarrow Y - X$ would seem reasonable, leading to a sequence



Assisted Mechanisms

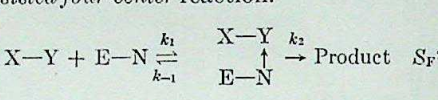
One might consider then that the bond making process 3, an electrophilic attack from the point of view of E, (E,N or E—N will be considered to be the attacking reagent in the following discussion), is an *assisted* process, assisted by the coordination of N. Similar reasoning would apply to addition reactions.[5]

Focusing on the substitution reactions possibly involving pre-rate determining attack by nucleophile, it would be difficult in many cases to characterize a given reaction involving X-Y and E–N into any one mechanistic category, a priori, because of the uncertainty involved in using isolability of an intermediate complex as a criterion for mechanistic assignment. The reasoning is as follows: the existent S_Ei nomenclature (*substitution, electrophilic, intramolecular*) should be limited to those reactions in which the attacking electrophile is contained within a stable molecule and the rate determining process is unimolecular and *assisted* by the coordination step. A *four-center* transition state is involved.



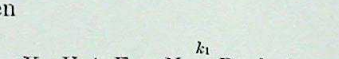
$$\frac{dp}{dt} = \left(\frac{k_2k_1}{k_{-1}}\right)(X{-}Y)\,(E{-}N)$$

This presupposes an isolable coordination complex, in equilibrium with the factors. If k_2 is large, and steady state conditions are approximated, this complex is not isolable and this *substitution* process can be described as an *assisted four-center* reaction.



$$\frac{dp}{dt} = \frac{k_2k_1}{k_{-1} + k_{-2}} \cdot (X{-}Y)\,(E{-}N)$$

If a completely concerted process is involved or the attack by E occurs so rapidly after the coordination of N to Y as to make consideration of a stepwise process meaningless then

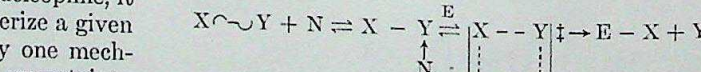


$$\frac{dp}{dt} = k_1\,(X{-}Y)(E{-}N)$$

This involves *substitution* by a *four*-center *bimolecular* process. Similar reasoning would apply to electrophilic assistance and internal nucleophilic reactions ($S_F{}^a$, S_Ni). These are the *limiting* cases to be considered. Obviously shading of one mechanism into another will occur, but the theory serves as a useful guide for further experimentation as indicated below.

Having established that the bonding properties of all four sites are important in a multi center cyclic transition state, it seems reasonable that the concept could be extended to noncyclic transition states where the nucleophile and electrophile as well as their respective sites of attack on the substrate might be separated. (Symbolized by A⌒⌣B.)

It is then conceivable to visualize a series of *assisted* reactions, $S_N{}^a$, $S_E{}^a$ and multicenter depending upon whether the rate determining process is nucleophilic, electrophilic, or leads to a multicenter (n-center) transition state, e.g.,



[5] Much is gained in considering addition reactions involving organometallic compounds by redefining attacking reagent and E and N. If R—M is considered the substrate X—Y, and the multiply bonded elements C=O, —C≡N, or C=N—, are considered E=N, then direct parallels may be drawn with the concepts developed by consideration of substitution processes.

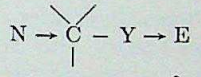
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It is important at this point to distinguish between complexing, or coordination, and assistance. Complexing, and coordination, focus on the process of replacement of ligand by ligand; assistance, on the other hand, induces an increased reactivity in an adjacent part of a molecule by a coordination step, and it is this increased reactivity to which attention is drawn in this paper. The chemistry of such coordinated ligands is a fresh and new field in the area of inorganic chemistry and there is an increasing trend toward considering alkyl and aryl groups attached to a metal as ligands.

Just as electrophilic assistance is expected to be evident in systems containing available lone pairs of electrons near the reaction site, one would expect nucleophilic assistance to occur where "electron deficiency" was present near the attacked site. The criterion of "electron deficiency" is met admirably by organometallic compounds, where the metal always possesses an incomplete octet or is capable of expanding its octet, and this would perhaps explain the sudden surge of interest in four-center reactions in such systems. The following paragraphs will suggest, however, that solvents play an important role in systems where assistance might be observable just as solvents play an essential part in determining the course of S_N1 or S_E1 reactions

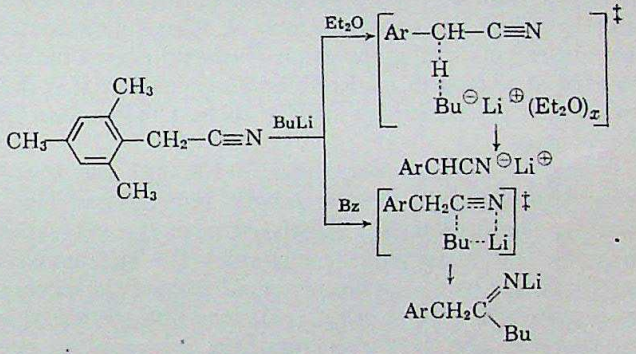
In the area of carbon chemistry, the concept of *electrophilic assistance* and/or catalysis is evident in the "push-pull" mechanisms of C. G. Swain (*22*). It has been demonstrated that in displacement reactions of organic halides in *benzene solution* there must always be both a nucleophilic (or pushing) agent to attack carbon, and an electrophilic (or pulling) agent to attack halogen in a rate determining concerted step regardless of whether the reaction is S_N1 or S_N2.



Electrophilic assistance in reactions has been observed and may be due to a solvent or added solute such as mercury or silver salts or other uncharged electrophiles. In order to illustrate this, consider the S_N1 reaction of triphenylmethylchloride with phenol and methanol, separately and in mixtures using benzene as the solvent. The kinetics indicate that the reaction with methanol is exactly third order, first order in halide and second order in methanol. When phenol is used, ether formation is 1/50 as rapid, but the reaction is still third order (second order in phenol). If the reactions were pure S_N1, one would have expected phenol to react faster than methanol since it is known to form stronger hydrogen bonds with halogens. The slower reaction of phenol is best explained by assuming that a solvation of the carbon is required in which phenol is less effective than methanol. When both methanol and phenol are present, only the methanol is consumed, but the reaction is many times faster than in the absence of phenol. The increase in rate is due to the greater electrophilic assistance of the phenol over methanol in the "push-pull" mechanism.

In protic solvents it is often difficult to observe the above effects, since few solutes are sufficiently more reactive to make up for differences in concentration; and it is only in cases where the solvent is relatively ineffective in both roles of nucleophile and electrophile and/or the assistor is exceptionally active that such effects would be kinetically observable. Thus solvent serves as an unseen assistor in many cases.

In a consideration of other specific solvent effects on electrophilic assistance, increased cation activity is found with a decrease in cation solvation, as would be expected. Parker (*23*) has been able to make some generalizations concerning cation solvation in the sense that cations appear to be more strongly solvated in polar solvents where the charge on the negative end of the dipole becomes increasingly localized, as on the oxygen atom in dimethylsulfoxide. However, if the negative portion of the dipole is dispersed (as in nitrobenzene), is a poor electron donor atom, or is subject to steric hindrance, the molecule becomes less effective as a cation solvator. (It should be noted that specific solvent-cation interactions tend to interfere with this generalization: *e.g.*, silver salts are more soluble in acetonitrile than water because of π bonding between the nitrile linkage and the silver ion (argentation).) That these cation solvation effects are important in organometallic reactions is indicated by the following (*24*);



In ether, where the lithium ion is highly solvated, the *highly independent butyl carbanion* serves to extract a proton from substrate—while in benzene, a poor cation solvator, the substrate serves as solvent and reactant, to yield the addition product.

Thus differences in solvation can lead to differences in observed rates or products. The relationship between the concepts involved here, and those proposed by Gielen concerning the cleavage of C-sn bonds[2] is obvious, as the following development suggests.

A consideration of some of the fundamental principles concerning solvation which have been developed in recent years also indicates where *nucleophilic assistance* is most likely to be observed (*23*). It is not surprising that kinetic evidence for nucleophilic assistance by anions has only recently been demonstrated, since Hudson and Saville (*25*) have correctly pointed out that anion solvation is usually greater than that of the cation, in the usual "kinetic" solvents which are protic in nature. This would lead to a masking or leveling of anion effects. Considering anionic assistors one could easily see that protic solvents strongly solvate anions through hydrogen bonding, thereby decreasing and leveling their activity (Cl^- versus Br^- versus I^-) and potential importance as nucleophilic reagents. When a dipolar aprotic solvent is used, solvation of the

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anion is less appreciable (no hydrogen bonding) and anion activity is increased as well as over-all differentiation of anionic activity. This is exemplified by the strength of halogen acids in dipolar protic solvents as compared to aprotic dipolar solvents. Thus, since solvation of anions in protic solvents is greater the smaller the anion, and bond strengths are greater the smaller the anion, the acids strengths are leveled. In dipolar aprotic solvents, the reverse is true, and anion solvation assists dissociation of the acids with the most polarizable anion, and weakest H-X bond, to differentiate acid strength. Similar arguments would hold for uncharged nucleophiles (Lewis bases).

A consideration of these concepts would lead to the conclusion that *nucleophilic assistance* would be most successfully sought and observable in aprotic or aprotic-polar solvents, such as dimethylsulfoxide, dimethylformamide, acetonitrile, or hydrocarbons.

In the cleavage of carbon-mercury bonds in various types of organomercury systems nucleophilic attack on mercury (assistance), in addition to the expected electrophilic attack on carbon, has been considered as a possible, and significant interaction (*26*), but in some cases it has been looked upon only as an alternative due to the lack of actual proof. Once considered, the idea has often been discarded on the basis of incorrect interpretation and scanty experimental evidence (*27*). Furthermore, a consideration of the fundamental principles concerning solvation discussed above makes it evident that such nucleophilic participation, if it did exist, was minimized by specific solvent interaction in many cases

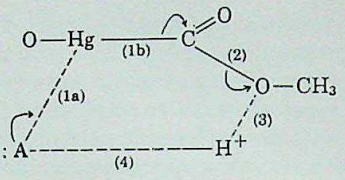
Thus, as Gielen's correlation for C-hg[2] and C-sn[2] cleavages suggest, whenever solvent impedes participation by the nucleophile associated with the attacking reagent (by solvation for example) the mechanistic pathway will be S_E2 in character, whereas if the solvent is a poor coordinator itself and does not solvate this nucleophile the pathway may be an assisted one (solvent itself may assist but this is difficult to detect kinetically).

In at least two cases definite kinetic evidence for assistance has been found in organometallic systems. Both of the reactions were conducted in dimethylsulfoxide (DMSO), a solvent which should enhance potential assistor activity. The first reaction involves the decomposition of carbomethoxy-mercury derivatives by weak acids.

$$QHgCO_2CH_3 \xrightarrow[X^-,\ DMSO]{HOAc} QHgX + CO + CH_3OH + OAc^-$$

Acetic acid does not decompose phenyl carbomethoxy-mercury (Q = $C_6H_5^-$) but the addition of chloride ion leads to immediate reaction. An investigation of the consequence of changing the nature of the added assistor led to the conclusion that the sequence of assistor activity was RSH > I^- > Br− > Cl^- > $(C_6H_5)_3P \rightarrow O$ > $(C_6H_5)_3P$, and C_6H_5OH. Note that neutral nucleophilic assistors are possible, suggesting that as in the electrophilic case solvents may also assist.

In a consideration of the electronic interactions responsible for assistance in this case, it is readily apparent that the ligand or mercury has three possible interactions with the metal: (*a*) σ-bonding via donation from a ligand lone-pair to an empty sp^x hybrid orbital of mercury previously occupied by solvent, (*b*) $d_\pi - d_\pi$ back-bonding involving a $5d^{10}$ orbital of mercury and an empty *d* of the ligand, and (*c*) π anti-bonding involving a filled p (or sp^x hybrid) orbital of the ligand and an empty *p* (or sp^x hybrid) orbital of mercury (*28*). The fact that phosphorus does not serve as an assistor is indicative of the importance of anti-bonding, π (*c*) as compared to $d_\pi - d_\pi$ back bonding, (*b*). One could conclude then that *2* lone-pairs are necessary for assistance in this case. We can picture such assistance as follows:



If step 3 occurred in a pre-rate determining equilibrium, then the observed rate law (eq. 29) should not be obeyed since acetate ion is produced in the reaction. Since sulfide-, Halide-, and the amine-mercury complexes are known and isolable (*29*), it seems likely that step 1*a* occurs before 2, 3.

$$\frac{d(CO)}{dt} = k_3\,(\text{“Hg”})\,(HOAc)\,(X^-)$$

Thus 1*a* can be conceptually divided into several phases, the most important of which appears to be π anti-bonding which gives rise to 1*b*. The latter could also be the result of induced polarization by the assistor. This results in increased freedom of the CO_2Me grouping and therefore increased electron density on the methoxyl oxygen. Attack by proton is thereby facilitated, or *assisted* by the ligand attached to mercury. The basic arguments involved are to be found in discussions of polarization theory and the so called *trans*-effect. In summary, whatever the source, the effect of covalency is to delocalize (render more diffuse) the electronic distribution around the metal atom and to weaken the carbon-metal bond. A more detailed discussion of the mechanism may be found in the original article on this reaction (*30*).

G. Wright has investigated the so-called deoxymercuration reaction which is similar in nature in *methanol* and found no evidence for halide assistance, undoubtedly because of the solvent used (*31b*). As explained above protic solvents hinder anionic nucleophilic assistance.

Work in these laboratories indicates that assistance may be also found in the reaction of tin hydrides with weak acids in dimethylsulfoxide (DMSO).

$$(C_4H_9)_3SnH + HOAc \xrightarrow[DMSO]{X^-} (C_4H_9)_3SnOAc + H_2$$

Here rate measurements suggest that the assistor activity is truly catalytic. Surprisingly the sequence of assistor activity is decidedly different than in the mercury case—Cl^- > Br^- > I^- > $(C_6H_5)_3P \rightarrow O$. It is interesting to note that Kuivila (*31a*) found *no evidence for such assistance when methanol was used as a solvent.*

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The concept of assistance explains a number of facts concerning organometal reactions. Thus, it appears that in many organometallic compounds the rate of cleavage of the metal-carbon or metal-hydrogen linkages is not a function of the acidity of the acid used alone but is also related to the ability of the atom to which the hydrogen is attached to coordinate with a metal atom. For example; Coates and Huck (*32*) have reported that the rates of cleavage of dimethylberyllium by active hydrogen compounds is in the order ROH > R_2NH > RSH. Also the cleavage of C—b[2] bonds is accomplished more readily with carboxylic acids than with HCl (*33*), since oxygen is a better donor than halogen.[6]

The rates of reaction of $LiBH_4$ with HA increases along the series H_5C_6, C_4H_5N, *t*-BuOH, CH_3OH, as HA is varied while the K_a's of the acids increases along the series C_4H_5N, *t*-BuOH, CH_3OH, C_5H_6 (*42*). Finally, Coates (*43*) has introduced a nearly identical concept to explain the different orientations of cleavages in the reactions $C_6F_5HgR + HCl \rightarrow$, and $C_6F_5HgR + Br_2 \rightarrow$. In addition of organometallic compounds (RM) to unsaturated linkages (>C=O, >C=N—, or —C≡N) coordination of the nucleophilic hetero-atom with the metal is a possible source of assistance for the subsequent attack and bonding processes involving the establishment of the R—C< linkages.[6]

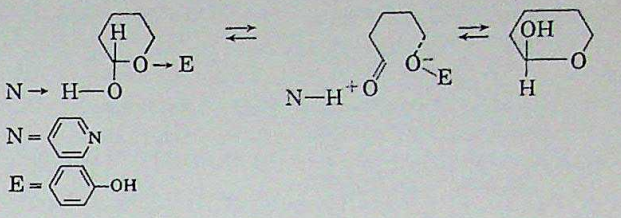
The practical applications of this concept of assistance seem very evident. It should be possible to increase the ability of an organometallic compound to donate a carbanion to a substrate or increase the ability of a metal hydride to donate a hydride ion to a substrate.

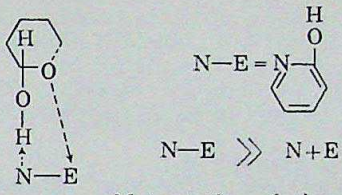
Brownstein (*44*) has shown that the C—M bonds in $(C_2H^5)_3Al$ and $(C_2H_5)_3Ga$ are weakened by solvation with ethers, and the b—H bonds in BH_4^- are weaker than those in BH_3 (*45*).

Conclusion

It is felt that this discussion points out the advantages to be gained by the application of the basic philosophies and nomenclature of the inorganic chemist to the field of reaction mechanisms involving organometallic compounds.

An over-all view of the concepts described above indicates an encouraging similarity to some of the arguments put forth by Swain (*36*), Bender (*35*) and others, in cases involving carbon as the focal point, or center of reaction. A survey of the literature indicates clearly that the concepts, and nomenclature, of electrophilic or nucleophilic assistance (often including catalysis), and multicenter processes (often including bifunctional catalysis, or electrophilic-nucleophilic catalysis) have been considered by physical-organic chemists. The systems are not always simple to interpret, as close observation[7] of the following examples would suggest.





Mutarotation of glucose (*36*)

$$CH_3CO_2H \rightleftharpoons CH_3CO_2^{\ominus} + H^{\oplus}$$

$$H^{\oplus} + RCONHR \rightleftharpoons RCONH_2^{\oplus}R \text{ (pre-equil.)}$$

$$CH_3CO_2^{\ominus} + RCONH_2^{\oplus}R \rightarrow CH_3COOOCR + NH_2R \text{ (slow)}$$

$$CH_3COOCR \xrightarrow[\text{fast}]{H_2O} CH_3CO_2H + RCO_2H$$

Electrophilically catalyzed hydrolysis of amides (*37*)

$$RCO_2C_6H_5 + N \xrightarrow{\text{slow}} \text{unstable complex} \xrightarrow[H_2O]{\text{fast}} RCO_2H + HOC_6H_5$$

Nucleophilically catalyzed hydrolysis of phenyl esters (*38*)

The conclusion is however, inescapable that nucleophilic assistance and multicenter reaction mechanisms are general throughout the periodic table. In fact it appears that such mechanistic features have not received the attention they deserve merely because most of our kinetic efforts to date have involved carbon centers, where these features are not likely to be distinct, given the electronic nature of a saturated carbon center. Indeed it is obvious that it is only at unsaturated carbon centers (*cf.* above examples) that even partial evidence can be gotten, and the protic solvents often used in kinetics have, as mentioned previously, done their part in masking the area. With the increased interest in the kinetic and mechanistic aspects of reactions at elements other than carbon in aprotic solvents, these ideas and concepts will be of increasing importance and usefulness.

[6] The exact sequence of donor ability among a set of ligands (O, N, S, X, etc.) will of course depend on orbital availabilities and the size and charge of the reference metal and ligand. Pertinent discussions of this problem may be found in references (*50*) and (*51*) where a division of various metals into *a* and *b* groupings, depending on ligand affinity, is made.

[7] The mechanisms involved in enolization, and ester or amide hydrolysis have been largely elucidated by deuterium isotope studies. There is increasing evidence which would suggest that a more careful examination of the origin of the observed isotope effects should be made. An excellent introduction to this complicated area is given in the articles by Bender (*35*, *38*).

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The Chemistry of Enamines

The class of compounds designated as enamines, although known for many years, has only recently gained recognition by organic chemists as an extremely important group of intermediates in organic syntheses. During the last decade, an increasing number of investigators have reported new ways by which enamines may be formed and in which they react. In the past few years, especially, a prodigious number of articles has appeared describing enamines and their advantageous use as intermediates and blocking groups in organic syntheses. The usefulness of enamine chemistry is growing so rapidly that this article will consider only those applications of enamines which the author considers most useful and of the widest interest.

The Nature of Enamines

The name enamine usually refers to α,β-unsaturated tertiary amines, $>C{=}C{-}N<$. Although this is the customary usage, the name enamine really implies any $C{=}C{-}N$ linkage. In this sense the name could be applied to the pyrrole family, the pyridine family and even aniline and its derivatives, all of which are certainly "ene-amines." Except for some indoles and pyrroles, however, such compounds do not in general display the typical properties of "enamines," probably as a result of the increased resonance in these fully unsaturated systems. We will concern ourselves in this article with α,β-unsaturated tertiary amines, the "enamines" that have evoked so much interest in the past few years.

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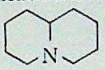
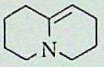
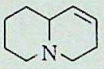
It should be at once apparent that enamines may be represented by two important resonance forms, the second of which is derived from the first by the conjugation of the unshared pair of electrons of the nitrogen atom with the double bond.

$$>\overset{\curvearrowright}{N}-C=\overset{\curvearrowright}{C}< \leftrightarrow >\overset{+}{N}=C-\overset{-}{C}<$$

Spectral Data and the Salts of Enamines

The conjugation of the unshared nitrogen electrons with the π-electrons of the double bond effects a bathochromic shift of 10–25 mμ as well as a substantial hyperchromic effect in the ultraviolet absorption (*1*), as illustrated in the table. Thus, comparison of the

Ultraviolet Absorption Data

	λ_{max} ($m\mu$)	ϵ_{max}
Saturated amines	213–216	1600–6100
α,β-Unsaturated amines	225–238	5100–9600
β,γ-Unsaturated amines	213–218	1700–5600
	215	3100
	228	5600
	214	2800

ultraviolet spectrum of an unsaturated tertiary amine with that of the corresponding saturated amine provides a convenient empirical method for differentiating between an α,β-unsaturated amine and other unsaturated amines.

The shift toward higher infrared absorption frequency accompanying the conversion of an enamine to its salt is due to the structural transformation

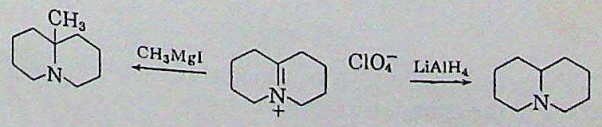
$$>C=\overset{|}{C}-N< \overset{HA}{\rightarrow} >CH-\overset{|}{C}=\overset{+}{N}< A^-$$

and may be used in the identification of enamines. The enamines themselves absorb in the C=C stretching region, near 1650 cm^{-1}, and their salts in the C=N stretching region, near 1680 cm^{-1} (*2*). The β,γ-unsaturated amines give no corresponding shift in this region. The shift toward higher frequency by α,β-unsaturated amine salts is accompanied by a more intense absorption than by β,γ-unsaturated amine salts.

The salts of enamines may be resonance-stabilized by participation of the two forms

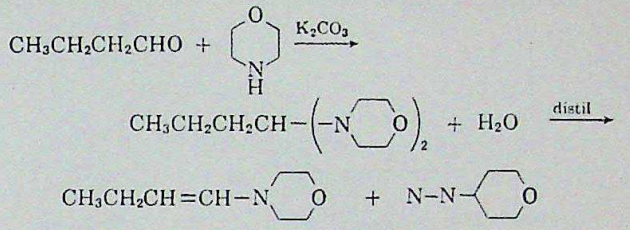
$$>CH-\underset{|}{C}=\overset{+}{N}< \leftrightarrow >CH-\overset{+}{\underset{|}{C}}-N<$$

and if this is so one might expect that they would be subject to nucleophilic attack at the α-carbon. Lithium aluminum hydride readily reduces the salts of enamines but not the enamines themselves (*3*). For example, $\Delta^{5(10)}$-dehydroquinolizidinium perchlorate can be reduced to quinolizidine. Furthermore, the salts of enamines react with Grignard reagents to give saturated amines (*4*).



Preparation of Enamines

The classical preparation of simple enamines (*5*) involves the mixing of an aldehyde and a secondary amine, in the presence of some dehydrating material which removes the water eliminated in the condensation of the amine and the aldehyde, to give a diamine with both amine residues on the same carbon atom. When the aldehyde has at least one hydrogen on the carbon atom adjacent to the carbonyl group, these diamines cannot, in general, be distilled without decomposition: they split off one mole of amine and yield an unsaturated amine. The formation of 1-morpholino-1-butene from butyraldehyde and morpholine is an example.



In this reaction, secondary cyclic amines give better results than dialkyl amines which are better in turn than aryl alkyl amines. Also, best yields are obtained when an excess of amine is avoided. Most simple aldehydes give enamines in 50–90% yield.

α,β-Unsaturated aldehydes also react with secondary amines to give ene-diamines (*6*)

$$R'CH=CHCHO + NHR_2 \xrightarrow{K_2CO_3} R'CHNR_2CH=CHNR_2$$

which decompose upon heating or exposing to air. At present, the most common method of preparing enamines (*7*) involves heating the ketone or aldehyde with a small excess of amine in benzene at reflux. A moisture trap is used to collect the water of reaction which forms an azeotrope with the benzene. Under these conditions, there is no evidence for the formation of the diamino compound and the reaction appears to be a direct condensation of one mole of the carbonyl compound and one mole of amine with the elimination of water.

Some amines show a preference for a particular type of carbonyl function (*7–9*); for example, piperidine forms enamines preferentially with steroidal aldehydes in the presence of steroidal ketone groups, whereas pyrrolidine is selective to C_3 carbonyls in steroids in the presence of C_{17} or C_{20} carbonyl groups. Thus formation of the pyrrolidine enamine could be used to protect a C_3 keto group in steroidal syntheses and the formation of a piperidine enamine of a steroidal aldehyde group could be used to protect it, provided the original carbonyl functions could be regenerated from the respective enamines.

The stability of acyclic enamines is not great; and upon treatment with aqueous acid and heat they readily decompose into the original carbonyl compound and amine (*5, 6*)

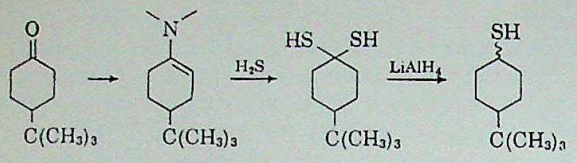
$$R_2N-CH=C< \xrightarrow{H_3O^+,\ \Delta} R_2NH + O=CHCH<$$

Treatment of enamines with hydrogen sulfide instead of aqueous acid gives gem-dimercaptans (*10*) which can be reduced to mercaptans with lithium aluminum hydride (*11*). This sequence has been used as

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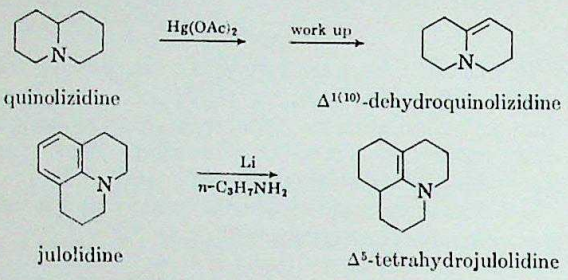
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the preferred method (*12*) of synthesis of 4-*t*-butylcyclohexylmercaptan (mixture of stereoisomers) from 4-*t*-butylcyclohexanone.



The aldehyde enamines are less stable than those derived from ketones; and those from α,β-unsaturated aldehydes are least stable.

Enamines in cyclic compounds have been prepared by the mercuric acetate oxidation of the corresponding amines (*3*, *13*), and by the lithium *n*-propylamine reduction (*14*) of aromatic amines. For example, quinolizidine has been oxidized by mercuric acetate to give $\Delta^{1(10)}$-dehydroquinolizidine in 60% yield; and Δ^5-tetrahydrojulolidine has been prepared by the lithium-*n*-propylamine reduction of julolidine, in 66% yield.



Reductions to Saturated Amines

Most enamines are readily hydrogenated catalytically (*5*, *6*) to saturated tertiary amines (except in the case of *N*-benzyl enamines, which, of course, lose the benzyl group during the hydrogenation).

$$RCH_2CHO + HNEt_2 \rightarrow RCH{=}CHNEt_2 \xrightarrow[PtO_2]{H_2} RCH_2CH_2NEt_2$$

$$RCH_2CHO + HNEtCH_2Ph \rightarrow RCH{=}CHNEtCH_2Ph \xrightarrow[PtO_2]{H_2} RCH_2CH_2NHEt$$

Thus primary, secondary, and tertiary amines may be made *via* enamines. Also ene-diamines may be hydrogenated to 1,3-diamines and may be reduced by sodium amalgam to γ-hydroxy amines.

$$R_2NCHR'CH{=}CHNR_2 \xrightarrow[PtO_2]{H_2} R_2NCHR'CH_2CH_2NR_2$$

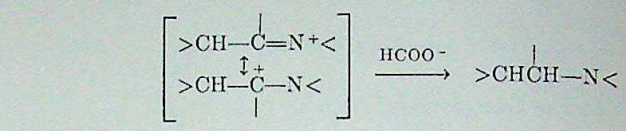
$$R_2NCHR'CH = CHNR_2 \xrightarrow{Na\ Hg} R_2NCHR'CH_2CH_2OH$$

Enamines may also be reduced by formic acid (*15*) in good yields. Addition of a slight excess of 98% formic acid to an enamine is accompanied by evolution of carbon dioxide and reduction of the double bond,

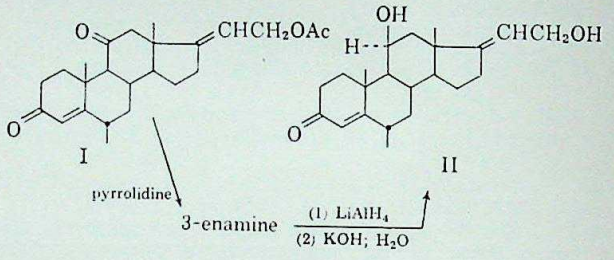
$$RCH{=}CNR'_2 \xrightarrow{HCOOH} RCH_2CHNR'_2 + CO_2$$

This method of preparing tertiary amines has been compared with the Leuckart-Wallach reaction. The enamines appear to be intermediates in this reaction (the reductive alkylation of amines by aldehydes and ketones in the presence of formic acid) and are more reactive under Leuckart-Wallach conditions than are the carbonyl component and amine separately.

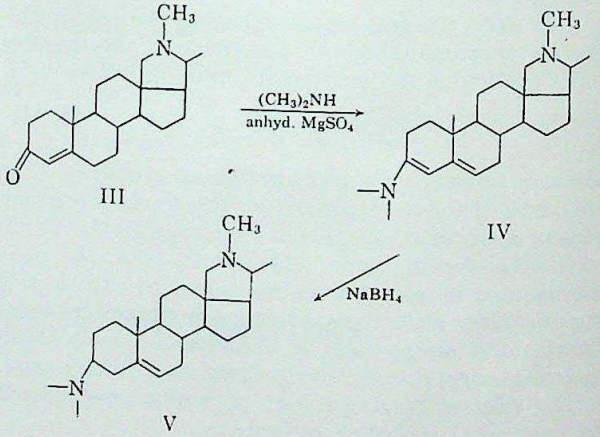
A study of the mechanism of this reduction (*16*) has led to the conclusion that protonation is followed by hydride transfer.



The fact that enamines are not reduced by lithium aluminum hydride, combined with the observation that pyrrolidine forms enamines preferentially with 3-keto groups in steroids has been used in the total synthesis (*9*) of 6α-methylhydrocortisone. The pyrrolidine enamine of 3,11-diketo-6α-methyl-4,17(20)-pregnadiene-21-oate (I) was treated with lithium aluminum hydride and the product hydrolyzed to 6α-methylhydrocortisone (II).



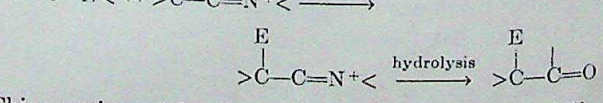
Enamines may be reduced chemically by $NaBH_4$. In the synthesis of conessine (*17*), the enamine intermediate (IV) from Δ^4-conanene-3-one (III) was reduced by $NaBH_4$ to conessine (V).



This was the first facile method reported for producing 3-amino-substituted steroids from 3-oxo derivatives.

Alkylations of Enamines with Halo-compounds

Considering once again the resonance structures for enamines, we might expect that they would readily undergo electrophilic attack at the β-carbon.

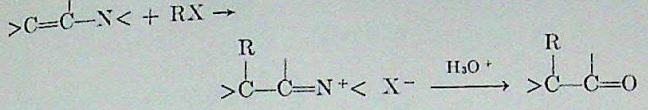


This reaction might also be thought of as a nucleophilic attack of the enamine on the substrate, E.

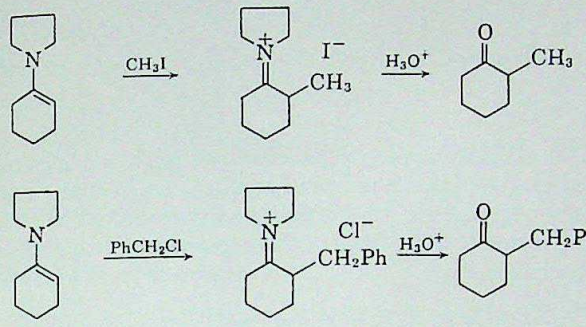
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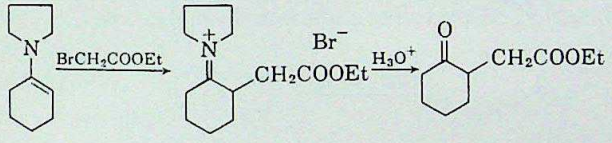
Probably the most important reaction of enamines is alkylation. The first type to be considered is the reaction of enamines with alkyl halides to give, after hydrolysis, 2-alkyl ketones.



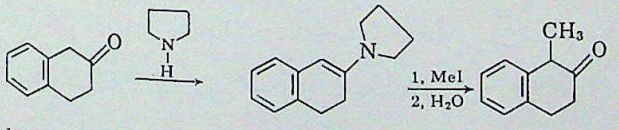
This reaction is exemplified by the alkylation (*18*) of the pyrrolidine enamine of cyclohexanone to give 2-methyl- and 2-benzylcyclohexanones.



Functional groups may be present in the halide as, for example, in the alkylation of the pyrrolidine enamine of cyclohexanone with ethyl bromoacetate.

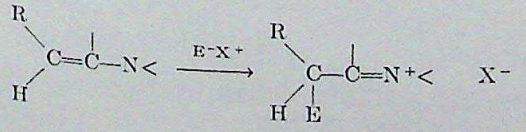


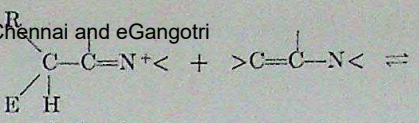
It is worthy of note that the above reactions as well as most other alkylations of enamines are readily terminated at the monoaddition stage. Thus, the conversion of a ketone to an enamine provides for easy monoalkylation in the α-position in very good yields. In fact, under the conditions used to monoalkylate the pyrrolidine enamine of cyclohexanone, the pyrrolidine enamine of 2-methylcyclohexanone gives mostly recovered starting materials (*18*). This low reactivity of substituted enamines is useful for example in the monomethylation of a β-tetralone (*18*) to give 1-methyl-2-tetralone. This procedure has found application in



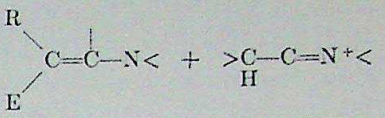
the total synthesis of *d*, *l*-dehydroabietic acid (*19*).

Since the alkylated enamine salts before hydrolysis are capable of giving up a proton to the parent enamine within the reaction system and thereby producing a new enamine, the restriction to monoalkylation must be due to a comparatively lower reactivity of the new enamine. In the following example E represents the electrophilic group:



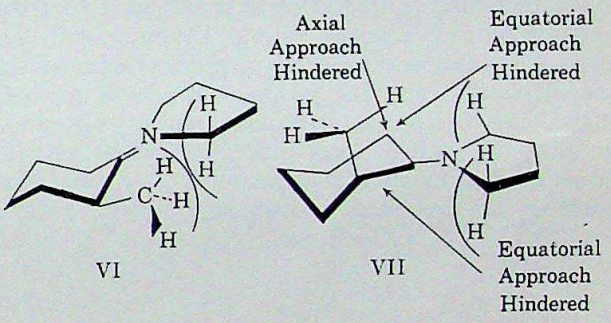


alkylated enamine salt — parent enamine



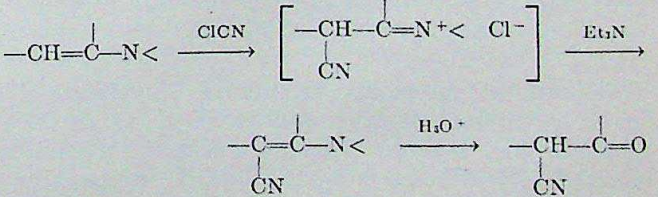
new (alkylated) enamine — parent enamine salt

Steric effects are believed to be responsible for the fact that alkylation of pyrrolidine enamines readily stops at the monosubstitution stage (*20*). Barton models of the pyrrolidine enamines of 2-methylcyclohexanone show that, in the transition state required for carbon alkylation, hydrogens on the pyrrolidine carbon alpha to the nitrogen interfere with the hydrogens of an equatorial methyl group (VI). This is because in the transition state for alkylation the enamine is converted to an imonium salt in which the bonds emanating from the nitrogen and from the alpha carbon are coplanar. If the methyl group is axial (VII), then attack is inhibited either by the same pyrrolidine hydrogens (equatorial attack) or by the axial methyl group (axial attack).



In addition to the ease of stopping at monosubstituted products, alkylation of enamines has the advantage that the mild conditions employed make it possible to alkylate carbonyl compounds which are labile to the strongly basic catalysts used in other types of alkylations.

β-Ketonitriles have been prepared (*21*) from enamines and cyanogen chloride in triethylamine.



This reaction is mild, easily controlled and gives good yields in most cases. The triethylamine is needed to neutralize the HCl which is eliminated from the salt of an enamine with a β-hydrogen.[1] Best yields may be obtained in this reaction from the pyrrolidine enamine,

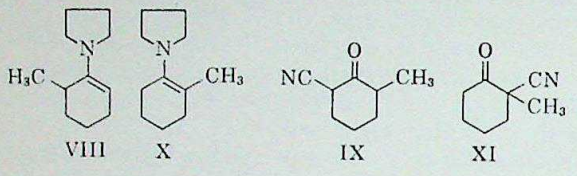
[1] The loss of a proton from the imonium salt is facilitated by the adjacent nitrile group as well as by the imonium function. If the resulting acid is not neutralized, it will compete for the basic cyanogen chloride.

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not only because it has the sterically most favorable transition state, but also because it is a stronger base and so competes more successfully with the triethylamine for the cyanogen chloride than do the enamines of the other common cyclic secondary amines, i.e., piperidine and morpholine.

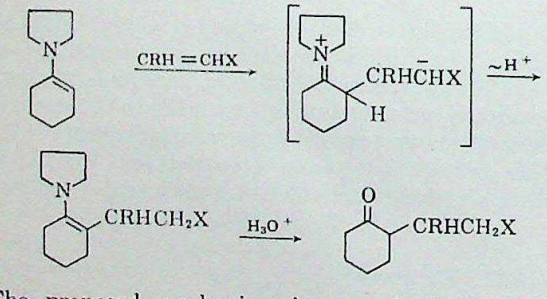
While the 2-methylcyclohexanone enamines do not react with methyl iodide under fairly stringent conditions, they do react with cyanogen chloride quite readily, even at low temperatures. Therefore, the steric requirement in this case must be much less than in other alkylations of enamines, presumably due to the linear structure of Cl—C≡N. Although the majority of the enamine formed from 2-methylcyclohexanone has the double bond oriented away from the methyl group (VIII) as evidenced by predominant formation of the 2-cyano-6-methylcyclohexanone (IX), there is some orientation toward the methyl group (X), yielding a small amount of 2-cyano-2-methylcyclohexanone (XI).[2]



VIII X IX XI

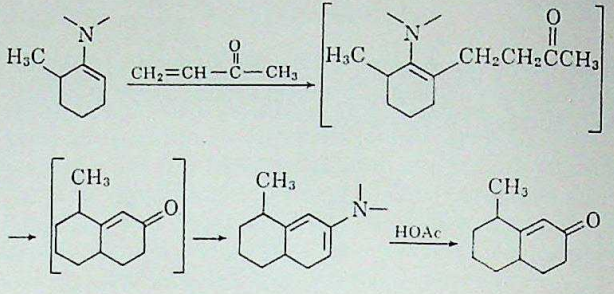
Alkylations with Unsaturated Electrophiles

Another kind of alkylation of enamines is that with α,β-unsaturated nitriles, esters, ketones, etc. This type of reaction is even wider in application than simple alkylations and the yields of products are quite high. The reaction can be applied to nearly any ketone or aldehyde with at least one α-methylene. An example is the alkylation of an enamine of cyclohexanone with an α,β-unsaturated compound in which X = $-COOR$, $-CN$, $-\overset{\overset{O}{\|}}{C}-R$, etc.

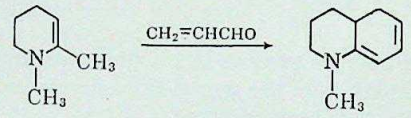


The proposed mechanism is normal alkylation followed by proton migration and hydrolysis to give tht monoalkylated ketone. This reaction has been applied to acrylic (R=H) and crotonic (R=CH_3) esters (X = $-COOCH_3$ or $-COOC_2H_5$), acrylo- and crotononitriles (X=CN), and vinyl (R=H) and propenyl (R=CH_3) methyl ketones (X = $-\overset{\overset{O}{\|}}{C}-CH_3$) yields of 45–85%.

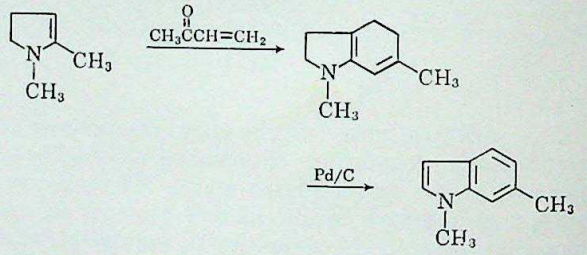
Methyl vinyl ketone has been condensed with substituted cyclohexanones to give 2-octalones. The following traces the detailed course of such a reaction, for which the reported yield is 56% (*22*).



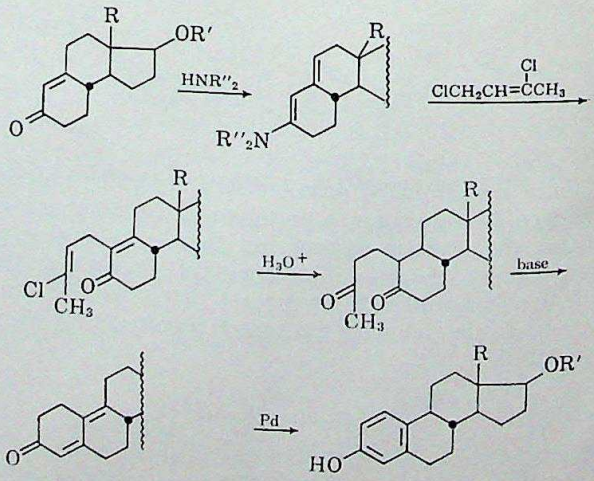
The alkylation of cyclic enamines with α,β-unsaturated electrophiles has found application in many and diverse syntheses. 1-Methylhexahydroquinoline has been formed (*23*) from 1,2-dimethyldihydropyridine and acrolein.



1,6-Dimethylindole has been synthesized (*24*) from 1,2-dimethyl-Δ^2-pyrroline and methyl vinyl ketone.



The enamine alkylation reaction has even been applied to formation of the A-ring in steroids. In the synthesis of 13β-propylnorestradiol (*25*) the enamine of the cyclopentanaphthalene (XII) (R=*n*-propyl) was alkylated with 1,3-dichloro-2-butene. The resulting chloride was hydrolyzed, treated with base, and then dehydrogenated.



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[2] It is conceivable that a tautomeric equilibrium between the two forms (e.g., (VIII) and (X)) might be established under the influence of conditions such as that pointed out in the discussion of restriction to monoalkylation:

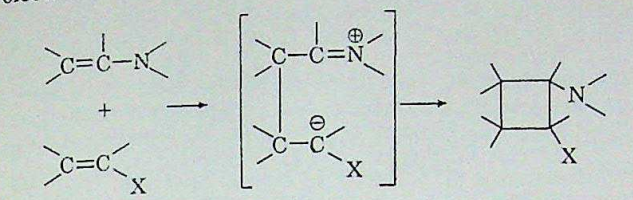
alkylated enamine salt + parent enamine → new alkylated enamine + parent enamine salt

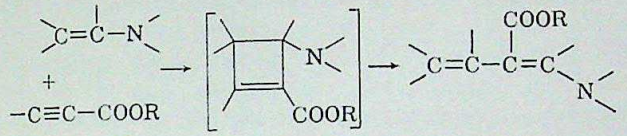
There has thus far been no evidence for or against such an equilibrium.

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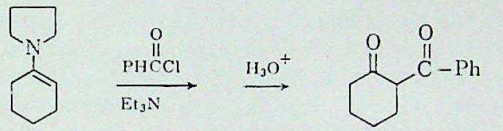
Double addition of enamines to α,β-unsaturated electrophiles to give cyclobutanes, and to conjugated acetylenic esters to form cyclobutene intermediates and eventually substituted dienes has also been reported (*26*). In the following illustration of this reaction the X signifies —COOR, —CN, —C(=O)—CH_3 and similar electron withdrawing groups.

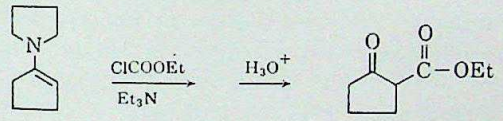




Acylations of Enamines

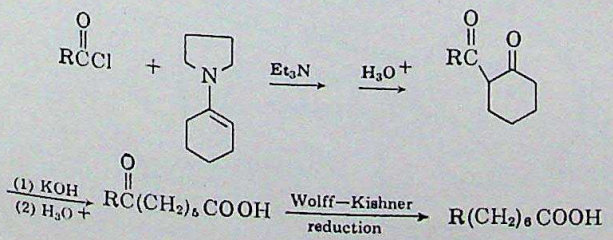
Enamines react with acyl chlorides to give 1,3-diketones after hydrolysis, and with ethyl chlorocarbonate to give β-keto esters (*18*).



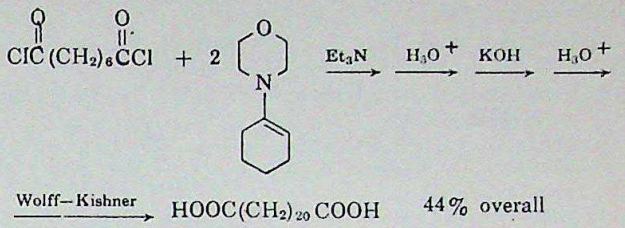


Yields are better than in the conventional base-catalyzed syntheses of diketones, and only the acylation of ketones with acid anhydrides in the presence of boron trifluoride gives comparable yields. This method has the disadvantage, however, that half of the anhydride is lost. Enamines derived from morpholine give the best results, e.g., 1-morpholino-1-cyclohexene and propionyl chloride give 2-propionylcyclohexanone in 86% yield, while with 1-pyrrolidino-cyclohexene the yield of 2-propionylcyclohexanone is only 63% under the same conditions (*27*).

The acylation of enamines has been used to extend carboxylic and dicarboxylic acid chains by five and six carbons (*28*). Conversion of an acid to an acid chloride and reaction of the acid chloride with cyclopentanone or cyclohexanone enamines yields an α-acyl ketone. Treatment of the α-acyl ketone with strong base (KOH) will open the ring and subsequent Wolff-Kishner reduction of the ketone will give the corresponding acid.

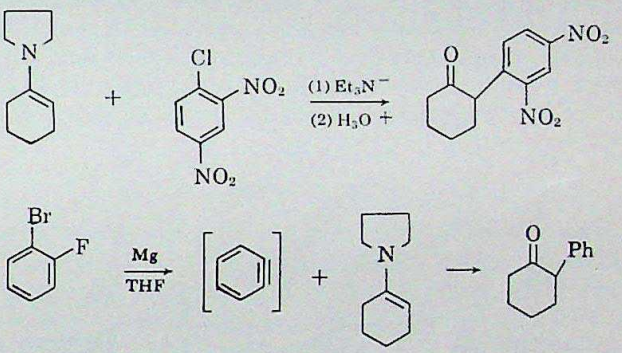


Similarly, dicarboxylic acids can be extended (*29*) by five or six carbons by converting them first to the monoester, and then to the ester-acid chloride, followed by acylation of the enamine, etc. Moreover, dicarboxylic acids can be extended by ten or twelve carbons by acylating two moles of the enamine with one mole of dicarboxylic acid dichloride, followed by the above described procedure.



Arylations of Enamines

Attempts to arylate enamines have met with poor results (*30*) except in the case of the very reactive halide, 2,4-dinitrochlorobenzene, which gives 2-(2,4-dinitrophenyl)-cyclohexanone from the pyrrolidine enamine of cyclohexanone. Arylations of enamines with benzyne type intermediates gives 2-phenylcyclohexanone, but in poor yields.



Summary

Enamines are now available through several synthetic routes of which the most common by far is the reaction of a carbonyl compound with a secondary amine with the loss of water. Because of their unusual polarization, both the enamines and the corresponding imonium salts serve as useful synthetic intermediates in a variety of chemical reactions, most notably alkylation and acylation. Following alkylation and acylation reactions, the product enamines may be hydrolyzed back to monoalkylated carbonyl compounds, β-diketones, β-ketoesters, β-ketonitriles and related species which are frequently more readily synthesized by this route than by conventional procedures. A detailed review of enamines, in English, is to appear shortly (*31*). An extensive discussion of alkylations and acylations of enamines (*32*) appeared after this paper was submitted.

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Chemical Laboratory, Poona, India, who first suggested the publication of this paper after it was presented by the author at a seminar.

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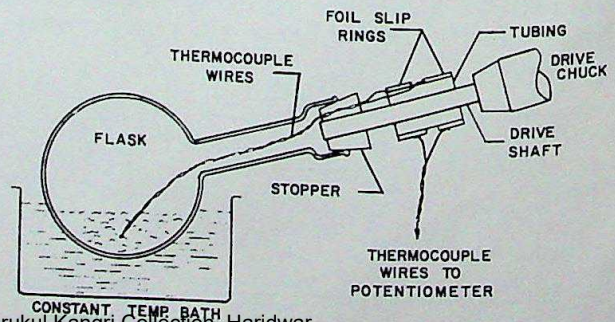
Device for Measuring Temperature in a Closed Rotating Flask

When heating substances in rotating heated flasks, it is nearly impossible to obtain a continuous temperature curve. A bulb thermometer can be placed within the flask, but it is difficult to read. A thermocouple could be used, but the flask rotation would twist the wires. Both problems can be overcome by using a slip ring and brush assembly in conjunction with a thermocouple.

A copper:constantan thermocouple was inserted into a flask with the external ends bared and extending 3–4 in. past the neck of the flask. An insulating length of tygon tubing of sufficient inside diameter to insure a snug fit was slipped over the drive shaft of the motor. The bared wire ends were extended along the tygon tubing, with one wire extending $1\frac{1}{2}$ in. beyond the other. Two bands of aluminum foil $\frac{3}{4}$ in. wide with a $\frac{1}{2}$ in. space between were wrapped around the tubing and wires so that each band contacted and depressed one wire. The bands were cemented in place.

Leads were attached to a potentiometer and extended to the flask. The loose ends were stripped of insulation. As the flask was rotated, touching the bared potentiometer leads (copper to copper and constantan to constantan) to the rotating slip rings permitted internal temperatures to be followed continuously.

The error introduced by the copper:foil:copper and constantan:foil:constantan junctions was reduced by placing the slip rings on the drive shaft where both were at the same temperature. If more precise measurement is required, copper and constantan slip rings should be used.



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Energy Relations in Teaching Organic Chemistry

Up until about 10 or 15 years ago elementary organic chemistry was taught as a very practically oriented subject. There were really only two major goals, synthesis and structure determination. Since that time there has occurred a gradual change in viewpoint, and this change is now more or less complete. Instead of being asked to classify reactions and memorize them, the beginning student is now usually taught the theory of a reaction before he is taught the experimental facts. There are sound arguments in favor of the older method of teaching: the most compelling is that theories may change; experimental facts will not.

The topic of this paper, "Energy Relations in Teaching Organic Chemistry," is not regarded by the author as an approach to organic chemistry, but rather a basis which will go along with any approach.

The amount of knowledge available in the field of organic chemistry continues to increase, and the old approach is no longer considered as being very practical by most teachers of the subject. The old approach is obviously sound, since almost all of us that today teach the subject in fact ourselves learned by the old method. The old approach is simply too time consuming and inefficient to cover the amount of material we would like to cover in the time that we would like to allot to it.

The goals of the elementary course have expanded, rather than changed, in the last several years. Structure determination and synthesis remain the principal occupation of a majority of practicing organic chemists, and they are useful and necessary tools to even the most theoretically oriented among us.

Usually organic chemistry is taught before physical chemistry, and such an order is assumed here. If physical chemistry is taught and taught properly before organic, as it is in a few schools, then presumably one need not teach energy relations in the organic course at all. It can be assumed the student knows about them, and they can be utilized. My personal experience has been that even after studying a moderate amount of physical chemistry, many students still lack a real grasp of energetics, and I feel this is because many teachers of elementary physical chemistry dwell excessively on infinite heat reservoirs, and pistons moving in cylinders and the like. The average organic student is left cold by this approach, since he is really interested more in chemistry than in plumbing. The connection between the two tends to be obscure to the student at this level.

There is at least one excellent textbook, "Organic Chemistry" by Morrison and Boyd, which has a very firm basis of energetics throughout. Other texts may refer to energetics to a greater or lesser extent, or not at all, but it is easy enough for the lecturer to add the material as he desires.

Presented as part of the Symposium on the Teaching of Elementary Organic Chemistry before the Division of Chemical Education at the 142nd Meeting of the American Chemical Society, Atlantic City, New Jersey, September, 1962.

Implications of Structure

We wish to apply energetics to both structures and to reactions. If, following Eyring, we think of the transition state in a reaction as a structure, which just happens to have a short life-time, then the study of reactions is reduced to a study of structures. It is necessary to emphasize to the beginning student that if the thermodynamics of a reaction are unfavorable, the reaction will not go, and further, that even if the thermodynamics are favorable, the reaction still may not go for kinetic reasons. Let us ask the question, what are the characteristics of reactions which proceed, as opposed to those which do not? These two reactions, for example, will seem very similar to the beginner, and he will

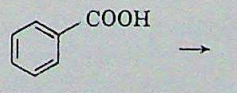
$$\text{R—OH} + \text{H—Br} \rightarrow \text{R—Br} + \text{HOH}$$

$$\text{R—OH} + \text{NaBr} \rightarrow \text{R—Br} + \text{NaOH}$$

have trouble seeing off-hand why the first will go and the second will not. The student already knows that acids react with bases to form salts plus water. The first reaction has an acid going to water, which can be viewed as related to acid-base reactions. The second reaction has a salt going to a base, which one wouldn't expect, in fact even the beginning student might predict that the reaction should go in the reverse direction, which it does. Bond energies and their use can be conveniently introduced at this point.

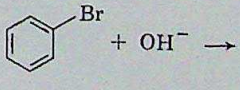
Keeping in mind a few rules of thumb, such as water, carbon dioxide, and salts are very stable and reactions which yield them as products are usually favorable, the student may decide that these reactions will go:

$$\text{R—COOH} + \text{R'OH} \rightarrow \text{R—COOR'} + \text{H}_2\text{O} \quad (1)$$



$$+ \text{CO}_2 \quad (2)$$

$$\text{CH}_2{=}\text{CH}_2 + \text{H}_2 \rightarrow \text{CH}_3\text{CH}_3 \quad (3)$$



$$+ \text{OH}^- \rightarrow \qquad + \text{Br}^- \quad (4)$$

Actually, the first reaction does go, at least to an equilibrium point, but the second and third go only in the presence of a catalyst and the fourth only under extreme conditions.

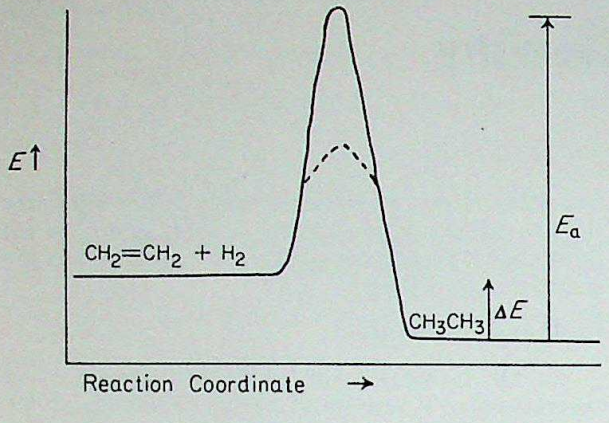
Use of Reaction Coordinate Diagrams

The hydrogenation of ethylene offers an example of a reaction which thermodynamics says should go, but

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which in the absence of a catalyst fails. The reaction coordinate diagram conveniently introduces the concept of activation energy and shows the function of a catalyst.



Within a limited series, stability of the reaction product will frequently parallel the stability of the transition state, and this concept can be widely used as long as the hazards involved are emphasized. Consider the example of the hydrolysis by an S_N1 path of a primary versus tertiary halide.

$$CH_3{-}CH_2{-}CH_2{-}CH_2{-}Br \rightarrow CH_3{-}CH_2{-}CH_2{-}CH_2C^{\oplus} \xrightarrow{H_2O} CH_3{-}CH_2{-}CH_2{-}CH_2{-}OH$$

$$CH_3{-}\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}{-}Br \rightarrow (CH_3)_3C^{\oplus} \xrightarrow{H_2O} (CH_3)_3C{-}OH$$

The reasons for the greater stability of the tertiary carbonium ion can be discussed, and then the reaction coordinate diagram can be considered (right column). Inspection of the reaction coordinate diagram shows that the tertiary halide is slightly more stable than the primary bromide, while the tertiary carbonium ion is quite a bit more stable than the primary ion. The energy change for the first step of the reaction (formation of the ion) is consequently greater for the normal case ($\Delta E^n > \Delta E^t$), and from the curves it is easy to see that the difference in activation energies parallels the difference in the energy of reaction, thus $E_a{}^n > E_a{}^t$.

Entropy Is Important

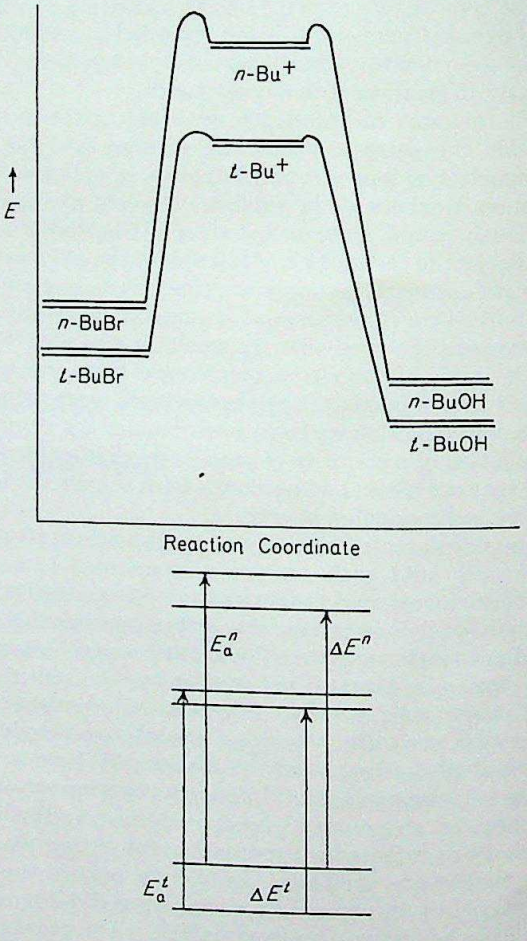
The difference between enthalpy and free energy can be pointed out, at least in a rudimentary way. The Boltzmann distribution and its temperature dependence can be examined, and these factors can then be combined to yield a rate equation. For a simple one step process of A + B → C, reaction is dependent on the molecules: (1) colliding, (2) having sufficient energy to react, (3) having the proper orientation to react.

$$\text{Rate} = (A)(B) \times (e^{\Delta E_a/RT}) \times (S)$$

An introduction to entropy and its relation to probability can be nicely illustrated by the carbene insertion reaction. This reaction is so vigorous that there is no selectivity between different kinds of hydrogens. A molecule like isopentane therefore reacts to give four different mono insertion alkanes, and these arise in strict proportion to the numbers of identical hydrogens, thus the numbers of identical hydrogens are as indicated, and the ratios of products are given by the ratios of these numbers.

$$(6)\ CH_3{-}\overset{\displaystyle (1)\ H}{\underset{\displaystyle CH_3}{C}}{-}CH_2{-}CH_3\ (2)\ (3)$$

Finally a more complicated case, say free radical chlorination, can be examined, in which both entropy and enthalpy must be considered. Here a tertiary carbon is more reactive than a secondary, which is more reactive than a primary, the relative rates of a single hydrogen being 4.4, 3.2, and 1 respectively under a specific set of conditions. The ratio of products will then, of course, be the product of the probability and energy terms, so that the chlorides isolated from the chlorination of isopentane will be in the ratio of 1 × 6:4.4 × 1:3.2 × 2:1 × 3 (for reaction at the carbons from left to right in the structure shown).



The use of energetics in the elementary course as discussed here is easy for the student to grasp, and if referred back to with sufficient regularity it gives the student a good grasp of the kinds of reactions which are reasonable, and those which are unreasonable, and it permits him to develop a judgment about reactions at an early stage which would otherwise come only after long experience.

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An Experimental Laboratory Course

With the ever increasing amount of chemical knowledge in the world has come a need to develop our best career students in chemistry as rapidly as possible.

The teacher of chemistry today is faced with the questions of what to teach and how best to teach it, as previous generations of teachers were. However, the problems today are more acute than in the past because of the vastly greater amount of theoretical, factual, and operational matter available. In this discussion we will concentrate on the operational or specifically, organic laboratory, instruction area as encountered at OSU.

Traditionally, our chemistry majors have had a laboratory course which required three three-hour laboratory sessions per week for three quarters. A laboratory manual was assigned and experiments from it were carried out routinely. After this course had been completed certain students did minor research problems, usually in their senior year, but this was not required of all.

In order to expedite the training of students we have started a different type of laboratory course which at present is optional for the chemistry major. Owing to limitations of space and money we can only allow eight or ten students to elect this course at the present. We hope to increase the possibilities in the future. The main features of this course are outlined and discussed below.

Each Student Has Laboratory Space of His Own. Thus at the end of a laboratory period a student need not put away his equipment. Experiments requiring more elaborate equipment and longer reaction times can be performed. Also students can come in at almost any time to do extra work. The only regulation on the latter feature is that there must be a graduate student (the assistant in the course) or some other responsible supervisor present.

The Type of Laboratory Apparatus Supplied Each Student Is Comparable to That Provided to Graduate Students Doing Research for Advanced Degrees. In this way a student learns to use and care for modern equipment. Thus better results may be obtained in many experiments and more sophisticated experiments may be run.

There Is No Assigned Laboratory Manual. Instead students are encouraged to buy their own books concerned with laboratory techniques and manipulations. No experiments are done on a "cookbook" basis. Rather, certain objectives are discussed in laboratory lectures and then each student in an individual conference decides what he will do. Often two or more students will set up experiments designed to test the effect of certain variables on a reaction, and each will carry out his part independently. In this way a research atmosphere is encouraged. Students are required to repeat certain experiments to see how well they can duplicate their own results and to see how much easier it is to run an experiment when they have had a little experience with it.

The Use of The Library Is Taught and Encouraged. In this way students learn to check on different ways of accomplishing certain objectives. Also, the quality of reports is improved.

Qualitative Organic Analysis as a Course Is Not Given. Rather, students are taught to use modern analytical instrumentation in the course of their work as well as traditional methods. Chromatography (column, vapor-liquid, and thin-plate) is encouraged as well as spectrographic (infrared and ultraviolet—even on occasion, NMR) methods.

Numerous Lectures on Laboratory Aspects of Organic Chemistry Are Given. From one to three hours of lecturing is done per week. In this way some of the experience of the lecturer is made available to the students. Also, the students are urged to compare notes on experiences in their own work.

Experiments Requiring Special Apparatus and Techniques May Be Assigned. All of the students do experiments which involve the use of liquid ammonia and hydrogen fluoride. Bomb reactions, vapor phase reactions, and ozonization are also almost universally used.

In All of the Work Done in this Course the Emphasis Is Placed on Doing Superior Work, Not Just on Getting a Certain Number of Experiments Finished. In this respect the student will generally repeat experiments in which his initial results were unsatisfactory. This often shows the student where he is making mistakes.

A few general remarks concerning the conduct of the laboratory work should be made. Throughout the entire course individual accomplishments and progress are given attention. At the start there is a great deal of personal supervision and emphasis is placed on acquiring the techniques involved in handling liquids and solids and their purification by conventional methods such as distillation, recrystallization, and column chromatography. The principles of separation of reaction mixtures into acidic, basic, and neutral fractions are discussed and illustrated, as are many experimental procedures during the course. Small scale, as well as medium and large scale, experiments are done.

Presented as part of the Symposium on the teaching of Organic Chemistry before the Division of Chemical Education at the 142nd Meeting of the American Chemical Society, Atlantic City, New Jersey, September, 1962.

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As the course progresses experiments requiring more unusual techniques are introduced (e.g., liquid ammonia, hydrogen fluoride, and others). During the last quarter emphasis is placed more on the research type of work and syntheses involving several steps are assigned, each student receiving an individual synthetic problem. In this phase of the work more independence of the student is encouraged as warranted. Students also present their experiences and results in seminar type oral discussions on occasion.

A few obvious difficulties in establishing such a course should be pointed out. Not only does it require considerable money but also space—since the laboratory space used for such a course cannot be used for any other purpose during the school year. It also makes great demands in time on the person who teaches this course. Unless a teacher with considerable personal interest in laboratory techniques and their continual improvement is available it would be better not to try to install such a course.

In the above description of the course, no specific reaction or experiment has been described. This omission was purposeful. In the final analysis the content of such a course must be worked out by the persons in charge. Their experience and judgment must be the determining factors in deciding what experiments should be done.

In conclusion, it should be stated that the gratifying part of giving such a course comes from the enthusiastic response of the students. It is heart-warming to see the amount of extra time given to this course by the students without exception. The minimum time spent would run about fifteen hours per week. Several students have gone out of their way to remark (after the course was over) that this was the most stimulating course in their educational experience.

A grant from the National Science Foundation was of great aid during the first year of this course as it made possible the services of Dr. George Axelrad in helping to get the course started.

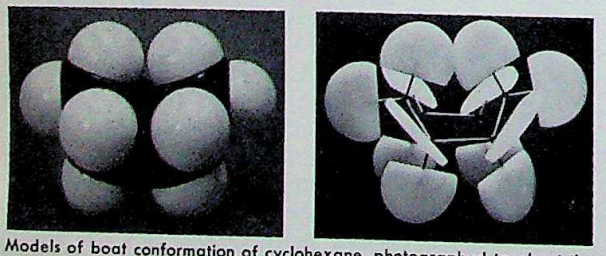
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Disc-Shaped Attachments for Dreiding-type Molecular Models

Spherical as well as rod-type molecular models possess both advantages and disadvantages. Thus, Stuart models (*Atomkalotten*) and similar types provide satisfactory illustrations of molecular shapes. The valency skeleton, however, is invisible, strained models are often mechanically unstable. Rod-type models such as those developed by Dreiding are excellent for the purpose of demonstrating bond angles and carbon skeletons; they do not indicate possible non-bonded interactions.

We have made an attempt to combine the advantages of both types in a simple and inexpensive fashion. We have constructed *disc-shaped* attachments fitting the Dreiding models. These attachments serve to represent the van der Waals radii of hydrogen atoms.

The discs were sliced from a polyvinylchloride rod of 2-in. diameter, corresponding to 2 Å on the scale of the Dreiding models—about $^1/_8$-in. thick. A segment corresponding to about 135° was removed in order to avoid hydrogen-hydrogen contacts at the same carbon atom.[1] A tight fit with a male or female end of the Dreiding carbon-hydrogen bond was obtained by drilling suitable holes in the discs.



Models of boat conformation of cyclohexane, photographed to about the same scale: left, Leybold model; right, Dreiding model with attachments for non-bonded radii of hydrogen atoms.

The models permit a view of the valency skeleton while at the same time illustrating possible non-bonded interactions. The discs may be turned about the C—H bonds so as to provide a maximum of steric interference with other groups. The models are mechanically stable and may be readily handled. Sizes are such that models can be used for lecturing purposes and for the preparation of scale projections, e.g., in X-ray work. Manufacture of a disc takes about twenty minutes. Various types of plastic may be used, including rubber.

Obviously, extensions to other monovalent atoms (e.g., halogen atoms) or groups (e.g., phenyl) can be made. It would appear that the usefulness of the above attachments lies in the fact that one can readily "extrapolate" from discs to spheres, whereas this is much more difficult from rods to spheres.

The author's thanks are due to Mr. Bauer, head of the instrument shop, for constructing the attachments and to Mr. Teegelaar and Mr. De Haas of the Laboratory for Inorganic and Physical Chemistry for making the photographs.

[1] Robertson, J. M., "Organic Crystals and Molecules," Cornell University Press, Ithaca, N. Y., pp. 227, 228, 1953.

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The Stereochemistry of (−) Menthol

An organic laboratory experiment

The trend in the first year organic laboratory at Haverford is to place less emphasis on short preparative experiments and more on longer experiments involving quantitative measurements. In these experiments the results are sufficiently complex that the student must devote considerable thought to their interpretation. Each student presents his interpretation in a short report answering the questions posed at the beginning of the experiment.

An experiment in the area of stereochemistry which has been quite successful is the determination of the relative configuration of (−) menthol.[1] In the course of this experiment, the student measures optical rotations, follows the rate of a mutarotation, evaluates the rate constants, and carries out a reaction involving asymmetric induction.

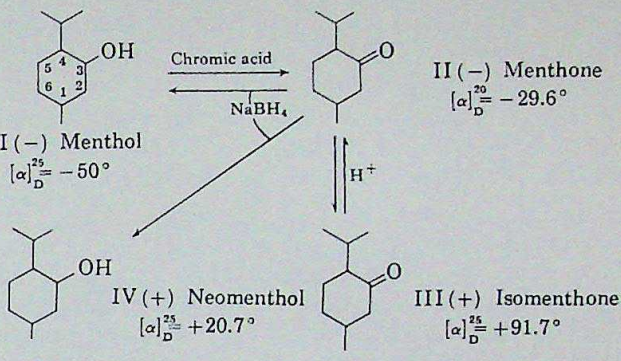
The student is given an optically pure sample of (−) menthol (I) and is asked to determine the configuration at C_3 and C_4 relative to that at C_1 using data from these experiments:

1. (−) Menthol, $[\alpha]_D^{25} = -50°$ is oxidized to (−) menthone(II) with chromic acid. If this oxidation is carried out carefully, the configuration at C_4 remains unchanged. Product rotation is determined.

2. A portion of the (−) menthone is treated with HCl in ethanol. The rotation is determined after a time t (three students are assigned each time). Each student places his point on a $\ln (\alpha_0 - \alpha_e)/(\alpha - \alpha_e)$ versus t plot. The acid concentration is such that the reaction is 90% complete in about three hours. Given that the C_4 epimer of (−) menthone, (+) isomenthone-(III), has a rotation of +91.7°, the student is asked to evaluate K_{equil}, k_f, and k_r for the reaction (−) menthone ⇌ (+) isomenthone. The rate constants k_f and k_r here include $[H^+]^n$; this may be separated and n determined if the class is large enough to use different acid concentrations.

3. The remainder of the (−) menthone is reduced to a mixture of (−) menthol and (+) neomenthol(IV) with sodium borohydride. The rotation of the product mixture is determined. The student is given the rotation of (+) neomenthol, $[\alpha]_D^{25} = +20.7°$, and is told that reduction of (−) menthone with hydride reagents bulkier than BH_4^- yields a product mixture of more positive rotation.

The reactions involved are as follows



The argument leading to the relative configuration at C_4 involves a straightforward application of the principles of conformational analysis. However, successful assignment of a configuration at C_3 depends on the student realizing that the products of the borohydride reduction are kinetically controlled. Even with this realization, the stereochemical arguments are quite sophisticated.[2] As a result, the student's interpretation of the data in assigning a configuration at C_3 is almost always deficient in some respect. After the reports are in, the paper by Dauben, *et al.*,[2] is assigned and carefully discussed in class. The difficulties in the interpretation of the data seem not to bother students; rather, they are pleased to face an experiment where the interpretation of results is not trivial. At the beginning of the experiment the student is given instruction in the operation of the polarimeter and is asked to derive the expression

$$\ln \frac{\alpha_0 - \alpha_e}{\alpha - \alpha_e} = (k_f + k_r)t$$

where α_0 = initial rotation; α_e = rotation at equilibrium; α = rotation at any time t.

The Experiment

The Oxidation of (−) *Menthol to* (−) *Menthone.*[3] Prepare a solution of chromic acid by carefully adding 7.2 ml of conc. H_2SO_4 to 90 ml of H_2O in a 250-ml Erlenmeyer flask and dissolving in the acid solution 15.8 g of sodium dichromate dihydrate.

Add menthol, 12.0 g, to the chromic solution, stopper the flask with a sound cork, cover the top with a paper towel, and shake the flask to initiate the reaction. Loosen the cork frequently to relieve any pressure build-up. The temperature of the reaction mixture should rise slowly (*ca.* 30 min.) to 55° as the flask is shaken vigorously. (If the temperature rises above 55°, cool in cold water. If it fails to reach 55°, heat gently on a hotplate.) The reaction mixture will remain near 50–55° for 15–20 min before the temperature starts to go down. The flask should be shaken vigorously during this time.

[1] A discussion of the stereochemistry of menthol is given by Eastman, R. H., and Noller, C. R. in Gilman, H., "Organic Chemistry," John Wiley, New York, 1953, Vol. 4, pp. 618–23. This source, however, gives the wrong rotation for (+) isomenthone. See Read, J. Chem. Soc., 1927, 1276.

[2] Dauben, W. G., Fonken, G. J., and Noyce, D. S., *J. Am. Chem. Soc.*, 78, 2579 (1956).

[3] Taken from the procedure in Gilman, H., ed., Col. Vol. 1, "Organic Syntheses," John Wiley, New York, 1932, p. 340.

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When the flask has cooled to about room temperature in an ice bath, extract the reaction mixture with 30 ml of ether, and then wash the ether layer with successive 30-ml portions of 5% NaOH until the ether layer is colorless. Wash the ether layer twice with 30-ml portions of water and dry it over anhydrous Na_2SO_4. Remove the ether by distillation from a 50-ml distilling flask using all the usual precautions. When the distillation temperature has risen above 45°, remove the hot plate and distill carefully with a microburner until the temperature reaches 180°. (This mixture tends to foam; heat gently on the side of the flask.) At this point *turn off your flame*, dismantle the condenser and receiver, and dispose of the distilled ether. Now distill without a condenser, collecting fractions in tared test tubes placed over the side arm. Collect the fraction 204–11°; determine weight and optical rotation.

The Mutarotation of (−) Menthone. Using an analytical balance, weight out exactly 2.000 g of menthone from the chromic acid oxidation in a 25 ml volumetric flask. Note the time and add in this order: 15 ml of ethanol (swirl), 5 ml of 5.0 N HCl and enough ethanol to fill to the mark. Mix immediately and at the time assigned you determine the rotation of the solution, again noting the exact time. Calculate the % composition of your mixture at time t and place your point on the ln $(\alpha_0 - \alpha_e)/(\alpha - \alpha_e)$ versus t plot.

Sodium Borohydride Reduction of (−) Menthone. Dissolve $NaBH_4$, 1.0 g, 0.02 moles, in a mixture of 10 ml H_2O and 15 ml MeOH in a round-bottom flask. Fit the flask with a condenser and add a solution of menthone, 4.0 g, 0.03 moles, in 10 ml of MeOH dropwise through the condenser. When the addition is complete, reflux the solution for 45 min. After cooling, add 30 ml of 5% NaOH slowly through the condenser and reflux the resulting solution 45 min. Extract the cooled reaction mixture with ether (twice with 30 ml), then extract the combined ether layers with water (twice with 30 ml), dry the ether layer over Na_2SO_4 and remove the ether by distillation with the usual precautions. The last traces of ether may be removed by using a microburner. When the temperature registers above 100°, stop the distillation and determine the weight and optical rotation of the clear oil remaining in the flask.

The time required for this experiment will depend on the number of polarimeters available. Laboratory sections of 15 using one polarimeter should be able to complete the experiment in 10 hr.

Average results for the experiment are given below. The rotations were determined at room temperature.

Yield of (−) menthone	65–70%
Specific rotation of (−) methone	−23° to −20°
Equilibrium composition of mutarotation mixture	25% (+) isomenthone 75% (−) menthone
Yield of menthols	75–85%
Composition of reduction mixture	40% (−) menthol 60% (+) neomenthol

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An Undergraduate Organic Experiment with Carbon-14

As new areas of knowledge in chemistry become important, the undergraduate curriculum must include them either as part of existing courses or as newly developed specialized courses; thus many departments have introduced an undergraduate course in radiochemistry. Many smaller colleges, however, have chosen the alternative of dispersing this study of radiochemistry into the traditional courses with emphasis on theory given in an upper level inorganic course and work on radioisotope technology dispersed through general, organic, analytical, and physical chemistry. The latter decision was reached at West Virginia Wesleyan College where we found an article by Phillips and Maybury (*1*) and a collection of experiments from THIS JOURNAL (*2*) particularly useful.

Organic chemistry is taught in the sophomore year and the organic radioisotope experiment could therefore presuppose some familiarity with counting equipment and an elementary understanding of radioactivity from the general chemistry course. On the other hand, quantitative experiments such as analysis by isotope dilution or molecular weight determination are reserved for the junior and senior years. In addition to those qualifications based upon plans for preceding and following courses we also wanted the organic experiment to fulfill the following requirements. First, the experiment should be open-ended and provide greater incentive for the students by having them identify an unknown. Second, it should help give an understanding of how isotopes are actually used. Because the organic laboratory was saturated with what was considered absolute essentials, a third restriction was imposed. The new experiment must cover reactions normally taught in the organic laboratory so it could replace said experiments, and students could then pick up radioisotope technology while studying the usual organic reactions. In addition to those experiments

[1] At present on leave at University College, Gower Street, London, England.

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referred to earlier, the literature has many good experiments for use in teaching analytical, physical and inorganic chemistry (*3–5*). The selection for organic is more limited, however, and we devised our own experiment which generated enthusiasm among the faculty and students.

The Experiment

The student is issued a sample of a small amount of ^{14}C labeled sodium acetate dissolved in acetic acid. The sample has been allowed to stand so that proton transfer from acetic acid to labeled acetate ion has resulted in the formation of labeled acid.

$$^{14}CH_3CO_2^- + CH_3CO_2H \rightleftharpoons {}^{14}CH_2CO_2H + CH_3CO_2^-$$

Converting the labeled acid into acetyl chloride,

$$^{14}CH_3CO_2H + PCl_5 \rightarrow {}^{14}CH_3COCl + POCl_3 + HCl$$

The acetyl chloride is used in a Friedel-Crafts acylation of benzene to produce acetophenone.

Reaction of the acetophenone with an alkaline solution of iodine gives iodoform which is separated by filtration and checked for ^{14}C content.

At the beginning of the experiment the student is informed that his acetate may not be labeled on the methyl carbon as in the above reactions. His sample may contain the carbon-14 in the carbonyl carbon. In this case the acetophenone would be labeled in the carbonyl position and the iodoform would not be labeled. In our actual experience where the iodoform is not purified, all iodoform products show some activity and because of this, the student is faced with the decision of whether the level of activity shows labeled form or contamination.

The above problem is resolved by a second experiment where the acetophenone is oxidized to benzoic acid. The acid is recovered by filtration and its activity is determined. Comparison of the activity of the iodoform with the activity of the benzoic acid leads the student to a decision regarding the location of the carbon-14 in his sample of acetic acid. The effect of the difference in molecular weight between the benzoic acid and the iodoform on the counts per minute for each sample is discussed in a qualitative way but no attempt is made to study this quantitatively.

This experiment was carried out with a class of 22 students. It required two laboratory periods (3–4 hours each) and the position of the carbon-14 was correctly placed by 20 of the students.

Suggested Procedure. The unknown is prepared for issuing to the student by dissolving a 0.6 mg sample of ^{14}C labeled sodium acetate (0.5 millicuries; specific activity 7.4 mc/mM) in 20 ml of acetic acid and allowing the solution to equilibrate by standing overnight. Each student is issued a 2 ml sample of the resulting labeled acetic acid.[2]

Acetophenone is synthesized by a modification of the procedure of Shuford, West, and Davis (*6*). A one-inch test tube is equipped with a Y-tube that has a reflux condenser in one opening and a cork in the other. The test tube is charged with 10 g of benzene and 8 g of phosphorus pentachloride. The acetic acid is added through the Y-tube in small portions and the reaction is allowed to subside after each addition. Thirteen grams of anhydrous aluminum chloride is then added to the reaction mixture in small portions. When the addition is complete and the reaction has subsided the mixture is refluxed gently for 30 min. and then poured onto 80 g of crushed ice plus 15 ml of concentrated hydrochloric acid. The acetophenone and unreacted benzene which separate from the water are diluted with 15 ml of ether and removed from the aqueous layer in a separatory funnel. The ether solution is washed with 15 ml of 5% NaOH, and 15 ml of water. After drying over Drierite, the ether is evaporated to give approximately one gram of acetophenone.

A portion (approximately 4 drops) of the acetophenone is dissolved in dioxane and treated with aqueous NaOH and iodine-potassium iodide to give iodoform. The yellow crystals are removed by filtration. The remainder of the acetophenone is oxidized by alkaline permanganate, and the benzoic acid obtained upon acidification of the solution is also separated by filtration. Procedures for each of these two reactions are available in most laboratory manuals. We used procedures described in Shriner, Fuson, and Curtin (*7*).

In preparing the samples for counting, a filtration apparatus similar to the one described by Radin (*8*) is used to give a standard filter cake that fits snugly into a planchet. Each planchet is in turn placed in the sample holder where the counts per minute are determined. Students should be advised that the count will depend upon the geometry of the sample and detecting device and that all samples should be placed in exactly the same position. Also the filter cake should be uniform and carefully placed in the planchet to avoid cracking. The counts per minute obtained will therefore depend upon the student's technique as well as the activity of the original acid. In our experience the active sample, whether iodoform or benzoic acid, gave five to ten times the number of counts that were obtained with the inactive sample and the active samples were generally between 50 and 250 counts per minute. An inexpensive scaler, timer, sample mount, and thin-window Geiger tube are satisfactory for this experiment. We used a set-up built around Tracerlab's SC-90 Decade Scaler with other parts taken from Nuclear Chicago's Model 7001 Nuclear Training System.

All reactions were carried out in hoods. Lacking sufficient space for each student to be assigned individual hood space, we set up the experiment on an assembly line basis. A battery of six condensers in Y-tubes was placed close together in one hood, where students could carry out the acetophenone synthesis. A second hood was set up for extraction and filtration and a third was used for the evaporation. Students started the experiments at one hour intervals in groups of six and although this made some rather late in finishing the synthesis, there were no other difficulties.

[2] Up to five samples of each of the labeled salts can be obtained, without a license, from Tracerlab, Inc., 1610 Trapelo Road, Waltham 59, Massachusetts or from any of several other suppliers. The cost is approximately $2.50 per student.

Acknowledgement

The author wishes to express his appreciation to the Atomic Energy Commission for providing the instructional equipment grant which made this work possible.

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He also thanks the organic laboratory assistant, Robert Maruca, and the students in the class for their constructive criticisms.

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(1) Phillips, D., and Maybury, R. H., J. Chem. Educ., 36, 133 (1959).
(2) "A Collection of Papers from the Journal of Chemical Education Related to Training & Experiments in Radioactivity," Nuclear-Chicago Corp., Des Plaines, Ill., 1959; see also, Radin, N. S., edit., "Radioisotope Experiments for the Chemistry Curriculum," Nuclear-Chicago Corp., Des Plaines, Ill., 1960, TID-6374.
(3) Roig, E., Rieckehoff, I. G., Russo, C. S., and Curet, J. D., J. Chem. Educ., 38, 350 (1961).
(4) Braunstein, J., and Young, R. H., J. Chem. Educ., 38, 31 (1961).
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Models Illustrating Rotational Isomerism in Aliphatic Chains

The usual atom models of the Stuart type[1] such as the Fisher-Hirschfelder-Taylor models[2] are not suitable for demonstrating rotational isomerism in aliphatic hydrocarbon chains since these models have free rotation about single bonds. We describe here a simple modification of the Fisher-Hirschfelder-Taylor models, which, without abolishing the possibility of rotation, gives additional stability to the staggered (*trans* or *gauche*) configurations of such hydrocarbon chains; the behavior of these models thus resembles that of the actual molecules in which the *trans* and *gauche* configurations are separated by potential barriers.[3]

Three holes (2 mm diameter and 8 mm deep) were drilled symmetrically into one face of an aliphatic carbon atom model (Fig. 1*a*) and three round-headed aluminum rivets ($^5/_{64}$-in. diameter and $^1/_4$-in. long) were inserted (Fig. 1*b*). Three conical depressions (5 mm diameter) were then drilled into one of the faces of the second carbon atom model (Fig. 1*c*) such that when the two models were connected together in a staggered configuration by means of the usual snap-fastener, the rivet-heads ($^3/_{16}$-in. diameter) fitted into these depressions. Figure 2*a* shows the use of two such modified carbon atom models to illustrate the stability of the staggered configuration of the ethane molecule. Since the height of the rivet-heads was only 1.1 mm, the two methyl groups could be rotated relative to each other from one staggered configuration to the next without becoming separated in the process. The standard snap-fastener retaining springs in these models proved strong enough to give ample rigidity to the staggered configurations. The above modifications to the standard Fisher-Hirschfelder-Taylor models were carried out using a rimmed triangular template which could be fitted over any desired face of a carbon atom model.

In order to prepare models illustrating the rotational isomers of aliphatic hydrocarbon chains it was of course necessary to modify two faces of each carbon atom model, except for those at the ends of the chains. We have found these models to be an invaluable aid in understanding the configurational problem and excluded volume effect in normal paraffins, considered recently by Smith and Mortensen.[4] Figures 2*b*, 2*c* and 2*d* show the three allowed types of rotational isomers of *n*-pentane discussed by these authors.

[1] Stuart, H. A., *Z. physik. Chem.* (Leipzig), B27, 350 (1934).
[2] Obtainable from Fisher Scientific Co., 633 Greenwich St., New York 14, N. Y.
[3] Mizushima, S., "Structure of Molecules and Internal Rotation," Academic Press, Inc., New York, 1954, p. 53.
[4] Smith, R. P., and Mortensen, E. M., *J. Chem. Phys.*, 35, 714 (1961).



Figure 1. Modification of the faces of the Fisher-Hirschfelder-Taylor carbon atom molecules

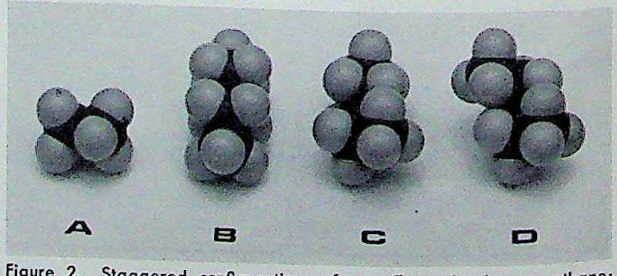


Figure 2. Staggered configurations of paraffin molecules: *a*, ethane; *b*, *c*, *d*, the three allowed types of rotational isomers of *n*-pentane; *a*, type 01; *b*, type 22; *c*, type 11. (The nomenclature is that of Smith and Mortensen.[4])

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Organic Chemistry in Ohio High Schools

Organic chemistry in high school is important since the majority of materials with which the laymen has daily contact are organic in nature and because it is so interesting and stimulating to the student.

The purpose of the present study is to determine the status of organic chemistry in Ohio high schools. The data was obtained from answers to a three-page questionnaire sent to the high school teachers listed by the Ohio Academy of Science as teachers of chemistry. Of this group, 312 teachers from 300 high schools responded. Data from the questionnaires was divided into four categories according to school enrollment in grades 10–12: (1) enrollments of 1–199, (2) 200–499, (3) 500–999, and (4) 1000 up. Approximately two-thirds of the responses are from schools with enrollments below 500. The school population range was from 4 to 3400 students.

One of the questions asked for the number of weeks devoted to organic chemistry. The responses are summarized in Table 1. Note that the responses vary from none to almost one semester (sixteen weeks), with a mean of 4.3 weeks. Taking into account the actual time spent in class, the smallest school group devotes 12.4 per cent of the high school course to organic chemistry; the three larger groups spend 11.3, 11.4, and 11.8 per cent, respectively, of the course time. The mean for the four groups is 12.0 per cent.

Presented before the Division of Chemical Education at the 142nd meeting of the American Chemical Society, Atlantic City, September, 1962.

Table 1. Number of Weeks of the Chemistry Course Devoted to Organic Chemistry

	School Size				
	1–199	200–499	500–999	1000 up	Total
Weeks	No.	No.	No.	No.	No.
0	1	1	1	4	7
1	1	2	...	2	5
2	15	10	7	3	35
3	17	23	16	13	69
4	17	30	16	11	74
5	9	8	6	10	33
6	17	18	9	8	52
7	3	2	1	3	9
8	3	2	1	1	7
9	2	...	2	2	6
10	3	...	...	...	3
11	...	...	...	1	1
12	2	...	...	...	2
13	...	...	...	...	...
14	...	...	...	...	...
15	...	...	...	...	...
16	1	...	...	...	1
No response	3	1	...	1	5
Not tabulated[a]	1	1	...	1	3
Totals	95	98	59	60	312
Mean	4.7	4.1	4.1	4.3	4.3

[a] Answers such as "varies" or "very little" could not be tabulated.

The percentage of laboratory time spent on organic chemistry varies as follows: It is highest in the 1–199 school population group, 15.0 per cent; 7.9 per cent in the 200–499 group; 10.6 per cent in the 500–999 pupil schools; and 12.6 per cent in the largest high schools. The mean for the four groups is 11.5 per cent.

The teachers were asked how many weeks of organic chemistry they would offer if time and facilities permitted. The answers indicate that they would like to allot five to six weeks. The averages follow: (1) 1–199 school size, 6.1 weeks, (2) 200–499, 5.3 weeks, (3) 500–999, 5.3 weeks, (4) 1000 up, 5.3 weeks, (5) mean, 5.5 weeks.

Many reasons were given for not presenting as much organic chemistry to the classes as desired. *Time* to include everything considered important is difficult to find. A textbook or laboratory manual is usually used as a guide as to what should be included in the course. The teacher soon discovers that, no matter how conscientiously he allots class time to each topic, it is virtually impossible to "squeeze in" everything. *Lack of necessary tools* and materials is said to limit the offering of much, if any, organic chemistry in some schools. *Inexperience* is the excuse of some of the respondents. The chapters on organic chemistry are usually the last in the textbook and the new teacher, plodding through chapter after chapter, finds the school year ending before he reaches the section on organic chemistry. *Educational backgrounds in organic chemistry* vary greatly among the teachers. Of those who commented, some teachers said they had had no course work in organic chemistry. One reported having a master's degree in the field and another said he is working toward a doctorate in organic chemistry. *Ability and interest of the students* decide how much organic chemistry will be covered in the class. What may be a mere taste in one section may reach the saturation point in another. The kind of school, and in some cases its location, may also help to determine the interests of the students.

A check list of 25 topics in organic chemistry was given in the questionnaire. The number of teachers who present the topics to their chemistry classes is shown in Table 2. Instead of including totals in Table 2, the topics are arranged in descending order of choice in Table 3.

The choices of the high school chemistry teachers do not correspond very closely to suggestions made by 110 Ohio college chemistry teachers in answer to another questionnaire about which topics in organic chemistry

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should be offered in high school. The college teachers would consider aliphatic and aromatic hydrocarbons under one title, hydrocarbons, whereas the high school teachers place most emphasis, evidently, on alkanes. The biochemicals concerned with foods are recommended by the college teachers for inclusion in the high school course, although only the carbohydrates are given important consideration by the high school chemistry teachers.

Asked whether organic chemistry should be an important part of high school chemistry, 78.3% of the teachers answered "Yes." Their reasons vary considerably. Some feel that high school chemistry should present an over-all picture and that omission of organic chemistry would simply mean not telling the whole story. A few stated that the field is simply too large to ignore. Others believe that interest demands inclusion of some organic chemistry—that it is a stimulus for the students. For every teacher who believes that organic chemistry should be reserved only for the college preparatory student, there is another who takes the opposite stand, that it should be presented only to the terminal student.

Table 2. Topics on Organic Chemistry Included in the High School Course

Topic	School size[a] 1–199 No.	200–499 No.	500–999 No.	1000 up No.
a. Alkanes	89	96	59	56
b. Alkenes	79	89	57	56
c. Alkynes	75	81	59	56
d. Halogen derivatives	79	86	56	54
e. Alcohols	88	93	56	56
f. Aldehydes	80	84	56	52
g. Ketones	54	59	44	49
h. Acids	82	85	56	55
i. Esters	83	90	55	53
j. Acid Anhydrides	47	33	17	23
k. Aromatic compounds	63	65	47	50
l. Soaps	74	70	47	50
m. Explosives	58	48	30	39
n. Ethers	70	75	47	54
o. Amines	33	34	25	33
p. Carbohydrates	77	64	40	47
q. Fats	65	55	36	39
r. Proteins	57	52	29	35
s. Textiles	55	47	28	35
t. Plastics	65	56	40	34
u. Enzymes	35	37	21	28
v. Vitamins	42	38	24	29
w. Hormones	23	21	8	17
x. Paints	30	24	14	14
y. Others:				
Agricultural chemistry	...	...	...	1
Chemotherapeutics	...	...	...	1
Cyclic Compounds	...	1	...	...
Dienes	...	1	...	...
Drugs	...	...	...	1
Dyes	...	...	2	2
Fuels	2	...	...	1
Insecticides	...	...	...	1
Medicinals	2	...	...	...
Paper	1	...	1	...
Petroleum	...	3	2	...
Rubber	...	2	4	1

[a] The total number of respondents was apportioned as follows according to school size: 1–199, 89; 200–499, 96; 500–999, 59; 1000 up, 56.

The high school chemistry teachers were asked if they felt a need for more course work as a background for organic chemistry. "Yes" answers were given by 174 teachers or 55.8% and "No" answers by 102, or 32.7%.

What the future for organic chemistry in the high school will be is uncertain. With more and more high schools using the Chemical Bond or CHEM study approach, less may be presented in the future. In the meantime, at least in high schools in Ohio, how much organic chemistry is offered to the students depends pretty much on the personal taste and background of the teacher.

Table 3. Ranking of Organic Chemistry Topics Included in High School Courses

Topic	Total number of votes	Per cent of total (300)
a. Alkanes	300	100.0
e. Alcohols	293	97.7
i. Esters	281	93.7
b. Alkenes	281	93.7
h. Acids	278	92.7
d. Halogen derivatives	275	92.5
f. Aldehydes	272	90.7
c. Alkynes	271	90.3
n. Ethers	246	82.0
l. Soaps	241	80.3
p. Carbohydrates	228	76.0
k. Aromatic compounds	227	75.7
g. Ketones	206	68.7
q. Fats	195	65.0
t. Plastics	195	65.0
m. Explosives	175	58.3
r. Proteins	173	57.7
s. Textiles	165	55.0
v. Vitamins	133	44.3
o. Amines	125	41.7
u. Enzymes	121	40.3
j. Acid Anhydrides	120	40.0
x. Paints	82	27.3
w. Hormones	69	23.0
y. Others	30	10.0

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Collected by
Alfred B. Garrett
Ohio State University
Columbus

The Flash of Genius, 15

Discovery of Insulin: Frederick Banting

Insulin, the chemical used to treat diabetes, was unknown at the beginning of this century. Its discovery was made by a 31-year-old Canadian doctor, Dr. Frederick Banting, in 1922. He had wanted to be a surgeon; but due to a lack of patients he had been forced to take a job teaching pharmacology at the West Ontario Medical School. One evening after preparing a lecture on diabetes, of which he knew very little, he happened to pick up the latest issue of a medical journal, *Surgery, Gynecology, and Obstetrics,* and read an article on the pancreas.

It was known that diabetes was due to some defect in the pancreas which resulted in sugar not being properly metabolized by the body and as a result it accumulated in the blood stream until death occurred. Banting thought of these facts and could not sleep—could it be that a healthy pancreas secreted something that aided the metabolization of sugar? It was known that the pancreas does secrete digestive juices; it was also known that a set of cells called the Islands of Langerhans shrivel in size as diabetes progresses. He had read that these island cells remain intact even though the pancreas duct is tied off causing destruction of that part of the pancreas which secretes digestive enzymes. Perhaps then these island cells are the ones that secrete a substance which burns sugar? As the story goes he jumped out of bed and wrote "tie off the pancreatic duct of a dog. Wait six or eight weeks for degeneration. Remove residue and extract."

He obtained meager space in the physiology department headed by Professor John J. R. MacLeod and set to work with the help of a young medical student, Charles Best. They anesthetized dogs, tied their pancreatic ducts, then analyzed their blood and urine for sugar to follow the degeneration of the pancreas. They also obtained a small amount of the extract from the island cells of the pancreas. They watched them carefully for development of diabetes and finally, in the ninety-second dog which they studied which had had its pancreas removed, they found it. The dog was dying of diabetes, but it revived when the injected it with a portion of the island cell secretion. This was their first success; they had succeeded in controlling the blood sugar. However, the blood sugar again increased and the dog died. It could probably have lived had he been given a continuous supply of this extract which Banting named "isletin."

Now the search was on for an adequate supply—they found it in the pancreas of animals being killed in slaughter houses and in the pancreas of unborn calves.

The next step was to find out whether this extract would also prevent diabetes in humans as well as in dogs. Their first human patient was a fourteen-year-old boy who was very ill with diabetes. An injection of the "isletin" revived him. Their next patient was a boyhood friend and medical classmate of Banting who was desperately ill with diabetes, Joe Gilchrist, who volunteered to let Banting perform necessary tests on him. He survived the first injection and then served as a "human rabbit" for tests to standardize the dosage.

All of this work was done in the laboratory of Professor MacLeod. At this point he entered the program in a very active manner. He worked out better methods of extracting the isletin and standardizing it. He renamed it "insulin." In January, 1922, a paper was read before the American Physiological Society by Banting, Best, and MacLeod announcing their discovery. In 1923, the Nobel Prize was given to Banting and MacLeod. In 1926, insulin was isolated in crystalline form by John Abel of Johns Hopkins University.

Banting, F., Best, C., and MacLeod, J., "The Effects of Insulin on Experimental Hyperglycemia in Rabbits," *American Journal of Physiology, lxii,* 1925, pp. 559–280.

Harris, S., "Banting's Miracle," Philadelphia, Lippincott and Co., 1946.

Thomas, H. and Thomas, D. L., "Living Biographies of Great Scientists," Garden City, L. I., Garden City Publishing Co., Inc., 1941.

There is nothing impossible about applying the mind in a more or less concentrated way for a good part of every day, if you set up conditions for it; and this is the straightforward explanation given by many prominent men for their achievements. In "Men of Mathematics," E. T. Bell quotes Gauss: "If others would but reflect on mathematical truths as deeply and continuously as I have, they would make my discoveries." And when Newton was "asked how he had made discoveries in astronomy surpassing those of all his predecessors, Newton replied, 'By always thinking about them.'"

John R. Platt
in "The Excitement of Science"

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Textbook Errors, 43

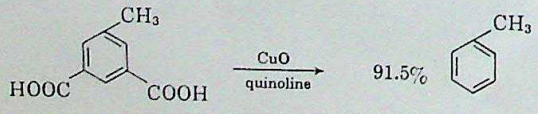
The Decarboxylation of Organic Acids

Many organic acids may be successfully decarboxylated, either as the free acid or in the salt form. However, simple aliphatic acids (except for acetic) do not give good yields of the corresponding alkanes, although many organic chemistry textbooks[1] list this as a general method for the preparation of alkanes. The condition usually given is that the salt of the acid should be heated with sodium hydroxide. However, Oakwood and Miller (*1*) heated the sodium salts of acetic, propionic, butyric, and caproic acids with equimolar quantities of sodium hydroxide and found that only sodium acetate gave a good yield of the corresponding alkane, methane (98.9%). Sodium propionate gave 44% ethane, but it was mixed with 20% methane and 33% hydrogen. Sodium butyrate and caproate gave 17 and 12.1% of the corresponding alkanes, respectively, but in each case about 38% methane. Berthelot (*2*) as far back as 1866 reported similar failures to prepare alkanes in this manner. Even textbooks which do not contain this error are seldom clear about which type of acids undergo the reaction. The following is a brief list, with examples mostly from "Organic Synthesis," of the more common types of acid which may be decarboxylated either as the acid or in the salt form of the acid. In general, the more stable the carbanion left behind when the carboxyl group cleaves, the more likely it is that the acid can be decarboxylated (*3*).

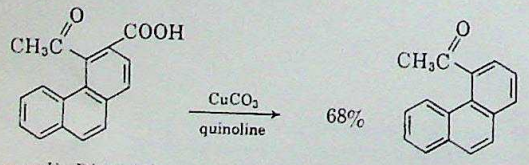
Aromatic Acids. Although benzoic acid itself is not easily decarboxylated (however, Mitscherlich in 1834 prepared benzene in this way), many other aromatic acids are, usually with copper or a copper salt, and quinoline.

Examples:

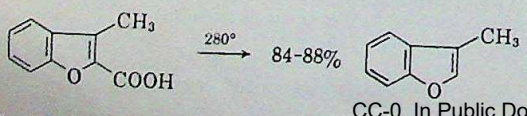
Benzene Ring (4):



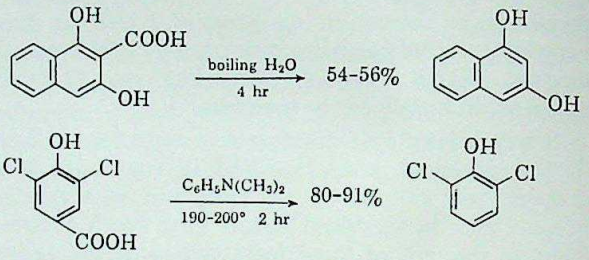
Fused Rings (5):



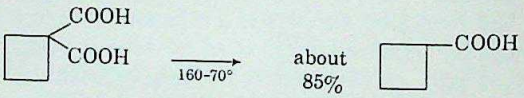
Heterocyclic Rings (6):



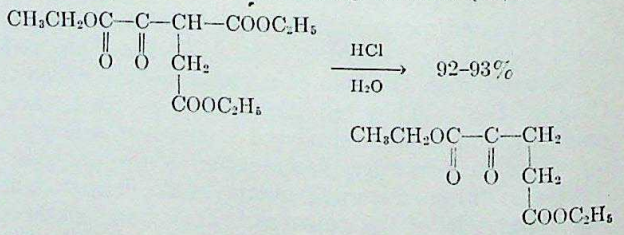
The statement that decarboxylation is facilitated by meta-directing groups in ortho or para positions (*7*) seems to be incomplete, since many aromatic systems not containing this feature decarboxylate readily (*8, 9*):



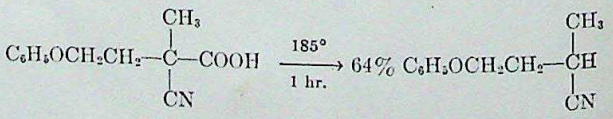
Alpha-Substituted Acids. By a Carboxyl Group. This type is the most common type of decarboxylation, since carbon dioxide is readily cleaved from compounds with two carboxyl groups on a carbon atom (*10*):



By a Carbonyl Group. This kind of acid is seldom subjected to decarboxylation, since the corresponding esters, which are prepared by acetoacetic acid-type syntheses, are themselves readily cleaved (*11*):



By a Cyano Group (12):



Suggestions of material suitable for this column and guest columns suitable for publication directly are eagerly solicited. They should be sent with as many details as possible, and particularly with references to modern textbooks, to Karol J. Mysels, Department of Chemistry, University of Southern California, Los Angeles 7, California.

[1] Since the purpose of this column is to prevent the spread and continuation of errors and not the evaluation of individual texts, the source of errors discussed will not be cited. In order to be presented an error must occur in at least two independent recent standard books.

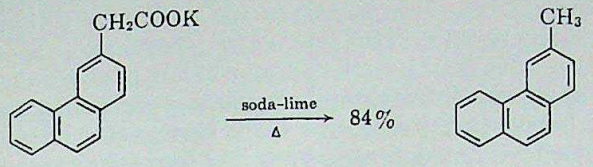
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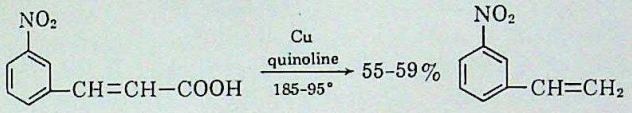
By a Nitro Group (13):

$$NO_2—CH_2—COONa \xrightarrow{80\text{–}85^\circ} CH_3NO_2$$

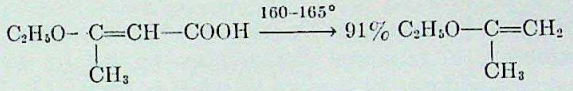
By an Aromatic Ring (14):



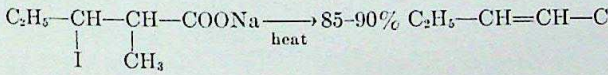
Alpha-Beta Olefinic Acids. Decarboxylations here have usually been carried out on acids with an aryl group in the beta position (cinnamic acid derivatives) (*15*):



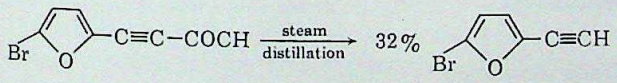
However, aliphatic compounds have also been used (*16*):



Beta-Substituted Acids. These decarboxylations are accompanied by eliminations; and it is likely that elimination occurs first, followed by decarboxylation, thus making this a special case of α-β olefinic acids (*17*).



Alpha-Beta Acetylenic Acids. Here also there is usually an aromatic group in the beta position (*18*):



Trihaloacetic Acids (19):

$$Cl_3CCOOH \xrightarrow[C_6H_5NO_2,\ 130^\circ]{KF} 70\%\ CHCl_3$$

The topic of decarboxylation reactions is too important to be completely ignored in a first-year organic chemistry course, although some of the preceding examples are probably too specialized to be taught in the first year. It would seem that the reactions of alpha-substituted acids should be included since they can be tied together theoretically—electron withdrawing groups facilitating the reaction. In addition, the decarboxylation of aromatic acids is important enough to be included; and it should be pointed out that while the reaction does work for acetic acid, it is not general for the higher fatty acids. The other reactions given above may be suitable for an advanced course.

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Peace Corps Science Teachers

Peace Corps Volunteers are teaching science today in elementary chemistry, secondary, college, and university class rooms around the globe. Additional Volunteers have been requested to teach science in 1963. In Latin America, for example, science teachers will be needed in the next school year for Ecuador, Costa Rica, British Honduras, El Salvador, Peru, Venezuela, the Phillipines, Ethiopia, Ghana, Nigeria, and Sierra Leone.

Intensive training at U. S. universities for overseas assignments will begin in June, July, and August of 1963. Some fifty campuses to date have been training centers for Peace Corps Volunteers.

For further information write the Peace Corps, Washington 25, D. C., to the attention of the Office of Public Affairs, or obtain a questionnaire from your local post office or contact your Peace Corps Liason Officer.

1963 Peace Corps Teachers Needed

	Chemistry	General science
Africa		
Ethiopia	5	10, 3 college level MA
Ghana	10	
Liberia		35
Nigeria	32	27
	2 college level MA	
Sierra Leone	2	20
Somali		5 elementary
Far East		
Philippines	15	30
Near East		
Turkey		22

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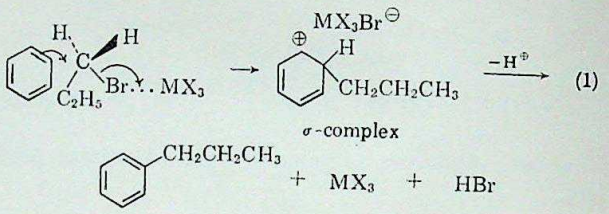
Textbook Errors, 44

Friedel-Crafts Alkylation

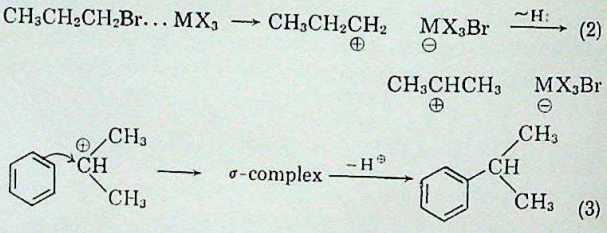
Friedel-Crafts alkylation is one of the reactions examined in some detail in many undergraduate organic chemistry textbooks. Most of these textbooks show that such alkylations involve carbonium ions as intermediates and that the ions often rearrange in the alkylation processes. Some of the textbooks[1] state that *n*-alkyl derivatives cannot be synthesized by the Friedel-Crafts reaction, or that they are formed in only minor amounts. That this is not always the case is evident from examination of the table. Thus, it has now been firmly established that in some alkylations with *n*-alkyl halides, *n*-alkylbenzenes are formed in significant amounts along with *sec*-alkylbenzenes.

The mechanistic treatment of the Friedel-Crafts reaction on the undergraduate level is unfortunately greatly oversimplified. This has become increasingly clear within the last ten years in which newer instrumental analytical methods (infrared and Raman spectroscopy, mass spectrometry, and vapor phase chromatography) have been applied to the re-examination of older available data and in current investigations.

Since the intervention of primary carbonium ions in Friedel-Crafts reactions would be expected to yield rearranged products exclusively, the formation of appreciable quantities of *normal* products must be otherwise rationalized. Thus, it is now thought that alkylations, in particular those involving primary alkyl halides, are nucleophilic displacements of the type suggested (1):



This view is supported by kinetic and other data (*6*). Formation of mixtures (table) may be due to simultaneous incidence of a more classical pathway (2), (3):



Variants of (2) and (1) include isomerization without ionization:

Suggestions of material suitable for this column and guest columns suitable for publication directly are eagerly solicited. They should be sent with as many details as possible, and particularly with reference to modern textbooks, to Karol J. Mysels, Department of Chemistry, University of Southern California, Los Angeles 7, California.

[1] Since the purpose of this column is to prevent the spread and continuation of errors and not the evaluation of individual texts, the source of errors discussed will not be cited. The error must occur in at least two independent recent standard books to be presented.

Examples of Friedel-Crafts Alkylation

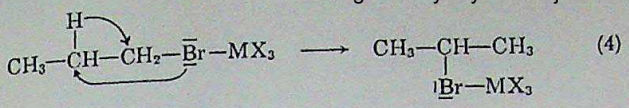
	Alkylating agent	Substrate	Catalyst	Temperature, °C	Analytical method[a]	Product	Reference
1.	*n*-PrCl	C_6H_6	$AlCl_3$	−18 to 80	IR; VPC	30-35% *n*-Prφ 65-70% *iso*-Prφ	(*1*)
2.	*n*-BuCl	C_6H_6	$AlCl_3$	0	IR; VPC	32-36% *n*-Buφ 64-68% *sec*-Buφ	(*1*)
3.	*n*-BuCl	C_6H_6	$AlCl_3$	80	IR; VPC	19-24% *n*-Buφ 54-63% *sec*-Buφ 14-27% *iso*-Buφ	(*1*)
4.	*sec*-BuCl	C_6H_6	$AlCl_3$	0 and 30	IR; VPC	*sec*-Buφ	(*1*)
5.	*sec*-BuCl	C_6H_6	$AlCl_3$	80	IR; VPC	35% *sec*-Buφ 65% *iso*-Buφ	(*1*)
6.	*iso*-BuCl	C_6H_6	$AlCl_3$	−18 to 80	IR; VPC	*tert*-Buφ	(*1*)
7.	*n*-BuCl	*m*-xylene	$AlCl_3$	35	D; DER; IR	63% *n*-BuAr[b] 37% *sec*-BuAr[b]	(*2*)
8.	*sec*-BuCl	*m*-xylene	$AlCl_3$	35	DER; IR	*sec*-BuAr[b]	(*2*)
9.	*n*-PrBr	C_6H_6	$GaBr_3$	35	IR	28% *n*-Prφ 72% *iso*-Prφ	(*3*)
10.	*n*-PrCl	C_6H_6	$AlCl_3$	35	D; DER	40% *n*-Prφ 60% *iso*-Prφ	(*4*)
11.	*n*-PrOH	C_6H_6	BF_3	60	MS; IR	*iso*-Prφ	(*5*)
12.	*n*-BuOH	C_6H_6	BF_3	60	MS; IR	*sec*-Buφ	(*5*)
13.	neoPentOH	C_6H_6	BF_3	60	MS; IR	96-97% *tert*-amylφ	(*5*)

[a] IR: Infrared spectroscopy; VPC: Vapor phase chromatography; D: Distillation; DER: Formation of solid derivatives; MS: Mass spectrometry.

[b] Isomerization accompanied these alkylations yielding 1,3,5-isomers rather than the 1,2,4-isomers.

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(4)

and synchronous alkylation and isomerization.

These mechanisms are not mutually exclusive. Friedel-Crafts alkylation with tertiary alkyl halides very likely involves the formation of a carbonium ion as an intermediate, while alkylation with a primary alkyl halide might take place either *via* (1) or (2 or 4) and (3). That portion of alkyl halide reacting by (2 or 4) and (3) would yield rearranged products while the remainder would yield normal products. For some alkyl halides, e.g., *sec*-butyl chloride (table, Nos. 4 and 5), formation of rearranged products may reflect an isomerization which *follows* alkylation (*1*).

Isomerization of alkyl halides by aluminum chloride or other Lewis acids is known to take place in the absence of arenes (*7*). It has been suggested that the presence of rearranged products in Friedel-Crafts alkylation with primary alkyl halides reflects *concurrent* or *prior* isomerization of the alkyl halide (*1*, *7*). Data on relative rates of substitution and isomerization are not yet on hand to confirm this view, although some predictions based upon the available data suggest that substitution with little rearrangement (isomerization) would be obtained by using as substrates more nucleophilic arenes (*8*)[2] or arenes in which an alkyl cation has ready access to the aromatic component (*8*). Nightingale and Shackelford's work (table, nos. 7 and 8) partially confirms this (*9*).

Older data which contradict some of the results listed in the table are still quoted in the literature with consequent confusion. It bears repeated emphasis: composition of mixtures determined on the basis only of boiling points, indexes of refraction and/or densities often are not valid (*10*). Even isolation of solid derivatives does not lead to unambiguous results; many cases are known in which a liquid mixture gives rise to but one solid derivative (*11*). An isomer or other component present in low concentration might be over-looked.

It is well worthwhile pointing out to students that use of an instrumental method of analysis is of itself no guarantee of a reliable analysis. Individual techniques have substantial limitations such that most often a combination of techniques must be relied upon. Additionally, most instrumental methods of analysis still require the availability of comparison standards which depend ultimately upon synthesis.

Other facts have come to light which explain some of the contradictory earlier data. For example, Roberts and Shiengthong have shown that part of the *sec*-butylbenzene formed in the alkylation of benzene with *n*-butyl chloride is due to the presence of *sec*-butyl chloride as a contaminant (as much as 17%) in the former compound (*1*). This is now readily understood as being due to intervention of the S_N1 mechanism in the conversion of *n*-butyl alcohol to chloride. The data on alkylation indicate that in addition to the nature of the alkylating agent, the basicity of the hydrocarbon, the nature of the solvent, the nature of the catalyst (including the presence of traces of water), and to some extent the temperature appear to influence the proportion of normal to rearranged product formed (see the table).

It is to be noted that disproportionations, transalkylations, and alkyl group migrations of primary alkylbenzenes—reactions which have features in common with alkylations—occur with little rearrangement, implying that carbonium ions do not intervene in all such reactions (*2*, *12*, *13*). In at least one case, it has been shown, using a ^{14}C tracer, that a superficially simple retention of skeletal homogeneity covers up a most interesting scrambling of the carbon atoms in an alkyl halide undergoing substitution (*14*), an "invisible" rearrangement as it were. The displacement mechanism has been invoked to rationalize some of these disproportionations and transalkylations. Recently, however, Streitwieser and co-workers have shown that another interpretation is necessary to explain some of these reactions (*15*, *16*).

In conclusion, the formation of rearranged alkylbenzenes in Friedel-Crafts alkylation, in particular with *n*-alkyl halides, is not as universal or as extensive as many organic textbooks imply. Although formation of rearranged products certainly is widespread, conditions and specific cases may favor the formation of the normal isomer in significant or preponderant amounts even if, thus far, no cases have come to light which are of synthetic utility.

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[2] Thus, yields of *n*-propyl derivatives of toluene, *p*-xylene, *m*-xylene, mesitylene, and pentamethylbenzene have been predicted as 49%, 54%, 75%, 91%, and 96%, respectively.

Note Added in Proof: Since the submission of this paper there has appeared one very significant and careful study which confirms the fact that appreciable percentages of *n*-alkylaromatics are formed in aluminum bromide-catalyzed alkylations (up to 50% for benzene and up to 88% for polymethylbenzenes) (Sharman, S. H. *J., Am. Chem. Soc.*, **84**, 2945 (1962)).

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Proceedings of the

California Association of Chemistry Teachers

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Ribonucleic Acid, the Simplest Information-transmitting Molecule

Man's ascendance to a singular position on this planet can be attributed to his acquisition and perfection of various special attributes. One of these is his ability to preserve and transmit information. The complex intellectual challenge to achieve this without the need of a human carrier resulted more than 5000 years ago in the development of symbols and scripts. In recent years attention has been focused on the fact that the problem of information transfer is not only an advanced intellectual development, but also represents one of the primordial features in the development of living organisms on the earth. Each cell transmits information to its daughter cells, and the information transmitted by sperm and ovum assures the continuity of evolution for the more complex organisms. We now regard the life process as resting on two primary pillars of function: replication and metabolism.

Metabolism with its associated sensory and motile functions represents and encompasses the machines and factories of the living state, while replication is assured by the blueprints or the microfilm of inheritable information. Proteins have developed as the ideal material for the metabolic processes, nucleic acids for the genetic functions. The proteins are 3-dimensional bodies of varied and specific shapes, and they make up the bulk of the cellular contents. The nucleic acids, on the other hand, function as ticker-tape like threads, and if they occur folded it is only for the sake of convenience or safekeeping. It seems from recent studies on flatworms that nucleic acids may represent the carriers not only of genetic but also of acquired information, or memory, and it is not excluded that they may play a similar role in the more complex nervous and mental centers of learning in the higher animals and man.

All cells contain the two kinds of nucleic acid, deoxyribonucleic acid (DNA), and ribonucleic acid (RNA). While the DNA may function exclusively as the storing house and primary template of genetic information, the RNA plays a variety of roles in transmitting this information to the metabolism factories in the day-to-day operation of the cell. Even the simplest cell contains thousands of functional proteins, all described in DNA records and coordinated and controlled by RNA molecules. It is therefore evident that cellular nucleic acids must be extremely complex in nature, and uninviting to detailed chemical study. Yet, it is the chemical detail which accounts for the function of these macromolecules, just as the detail of each letter determines the meaning of words and sentences.

Whenever scientists are faced with a complex natural phenomenon they attempt to simplify it, or they search for the simplest examples of the given phenomenon. In this sense, the viruses which generally lack all metabolic activities represent ideal objects of study for those interested in nucleic acid function. Viruses may be regarded as genetic units of nucleic acid, endowed with a specific protein coat for its protection in transport from cell to cell or from host to host. They become functional only within a host cell whose machinery they can commandeer for their replication. The amount of information which a virus particle must carry is variable, as we will see, but it is always very much less than that carried by a complete cell, and the obvious consequence of this is that there is much less nucleic acid in a virus than in a cell. Thus, viruses probably represent the best material for a chemical approach to the problem of genetic information transfer.

Viruses may contain either DNA or RNA. All RNA containing viruses seem to contain one molecule of RNA, of a molecular weight of about 1.0–2.5 million which means that according to current concepts which we will explain later, they contain 1000–2500 genetic letters. This seems to be the minimal amount of information to describe the structure and function of a virus. The DNA viruses range from this same size up to 100 times this size, and many of the bigger ones are known to perform much more complex functions in invading thick-walled bacteria and forcing the host cell into new metabolic pathways.

The Chemical Structure of Nucleic Acids

For obvious reasons, chemical research has been concentrated on the RNA and DNA of the simplest viruses. Both of these macromolecules represent unbranched sugar-phosphate-sugar-phospate. . . chains,

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the sugar being ribose for RNA and 2 deoxyribose for DNA, and the phosphate forming diester bridges between the 3′ and 5′ positions of adjacent sugars (Figure 1). The feature that makes these molecules functional is the attachment of one of four possible purines or pyrimidines at the aldehydic 1′ position of each sugar residue (see Figure 1). The order of these so-called bases appears to be the primary feature of genetochemistry. Three of them, adenine, guanine, and cytosine are shared by RNA and DNA. Since these do not carry an electric charge between *p*H 4 and 9, the term bases is really a misnomer, just as the term nucleic acids is a misnomer, since these occur and are stable only as the salts or nucleates, but not as the free acids. The fourth component, no base at all, is uracil in RNA and 5 - methyluracil (thymine) in DNA. The complete monomer unit of base-sugar-phosphate is termed a nucleotide, and it may be looked at in at least two different ways. Certain enzymes degrade nucleic acid by splitting the phosphate -3′ ribose bond and thus yield 5′ phosphorylated nucleotides; on the other hand, acids, alkali, and other enzymes split the other way and thus produce 3′ phosphorylated nucleotides. Under certain conditions the phosphate groups on the 3′ ribonucleotides may partly rearrange to the 2′ position. The availability of the 2′-OH group next to 3′ phosphate ester bridge is responsible for the great alkali sensitivity of RNA (in contrast to DNA), and this may well have been the chemical cause for an evolutionary advance from RNA to DNA as the primary genetic material of all organisms.

As stated, the sequence of four symbols along the polymer chain appears to determine its function. What can we say and learn about such sequences? Unfortunately there is as yet a great lack in methods for the sequential analysis of polynucleotides. And even if good methods were available the length of the chain and the lack of characteristic features (such as rare letters in an alphabet) will make sequence analysis of a viral RNA an extremely difficult task which may require many decades for its completion. Concerning the virus RNA which is studied most intensively in our laboratory (that of the tobacco mosaic virus) we believe we know one nucleotide at the left end, and four at the right end of the chain of 6400, and less is known about other viral nucleic acids (*1–3*). Intensive work is going on with a class of small RNA molecules (80 nucleotides long), the so-called transport-RNA (or s-RNA). This RNA has special features facilitating sequence analysis from one end, and information about one-tenth of the chain is now being accumulated for some of these agents by P. Berg and his collaborators at Stanford University (*4*).

Another approach is not from the ends, but through the determination of groups of "odd" sequences. Most nucleic acids are composed of similar amounts of purines and pyrimidines and one can calculate the probabilities of these occurring in groups of 2, 3 or more of the same kind, etc., for a random polymer. In a specific and functional polymer such bunches of the same nucleotide, or of neighboring purines or pyrimidines would differ in frequency from that calculated and such differences would represent characteristic features of a given nucleic acid. Methods to determine the frequencies of neighboring purines or pyrimidines and of other specific sequences are now available, and interesting data are being accumulated, as shown by the following example. Although we know that the RNA of two different strains of a virus must differ (for it is the RNA that contains the information describing both the similarities and the differences between these strains), no differences were detected in the nucleotide composition of different strains of TMV. However, structural differences of the type discussed above (frequency of bunches) could be demonstrated among several of these strains (*5*). A completely different technique has enabled scientists in Kornberg's department to determine the nearest neighbor frequency of DNA, again a highly specific chemical feature of this class of macromolecules (*6*).

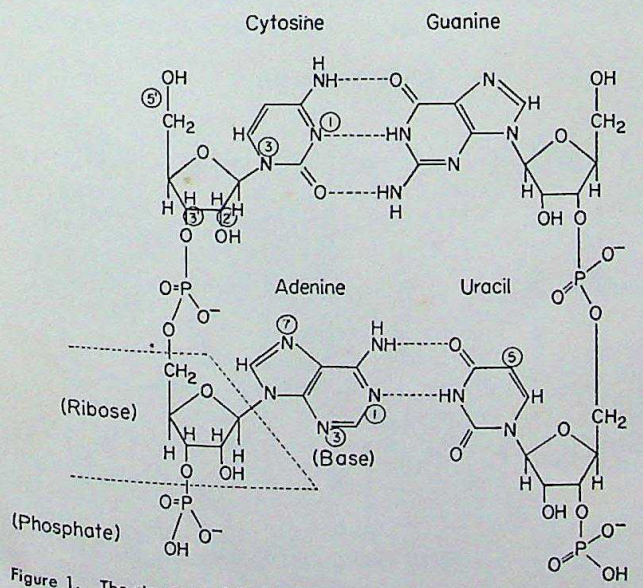


Figure 1. The structure of 2 dinucleotides, cytidylic 3′-5′ adenylic acid, and guanylic 3′-5′ uridylic acid. The three building blocks (phosphate, ribose, base) are delineated. The bases are shown H-bonded in pairs, as they tend to be in polynucleotides.

Chemical Modification of RNA and Mutagenesis

While we are as yet unable to determine long nucleotide sequences, we do have methods to alter them by chemical means. Among these methods, which include alkylation, halogenation, etc., the most fruitful has been the deamination resulting from treatment with nitrous acid. When applied to viral nucleic acid this as all other modification reactions causes gradual loss of its biological function, an average RNA molecule being inactivated when about two of its 6400 nucleotides have become chemically altered ("hit") (*7*). What made this study so important was the discovery that most of the surviving molecules gave different symptoms than the original virus, which means that they were mutants, resulting from the chemical modification of the nucleic acid (*8*). If we now look at the specific effect of deamination of the aminopurines, adenine and guanine, we observe that the resulting deaminated purines are unnatural nucleic acid constituents. In contrast the deamination of cytosine yields uracil, a natural component of RNA (Figure 2). Thus deamination of RNA, but not of DNA may produce chemical variants of the same species of mole-

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cules, and it appears probable that many of the observed mutants are progeny of such molecules in which 1, 2, or 3 cytosines have been changed to uracil. As we will see later this means of producing with high probability a specific change of the genetic script has proven of considerable importance in the elucidation of the nature of the code which relates RNA structure to protein structure.

Before we can enter more deeply into the discussion of the nature of the code and its change by mutation, we must first describe the present concepts concerning the function of the genetic material, or the reading of the information. Intelligent information transmittal requires an intelligent receiver. Both writing and reading are active processes. In contrast, chemical information script must through its chemical structure make itself read—writing must force reading. This has proven to be realized by the chemical nature of the bases. As it was first formulated by Watson and Crick on the basis of available analytical and X-ray scattering data, a remarkable fit and hydrogen bonding affinity makes the 6-amino purine (adenine) bind to the 6-ketopyrimidines (uracil and thymine), and the 6-ketopurine (guanine) to the 6-amino pyrimidine, cytosine, particularly if these are in polymer linkage (Figures 1, 3). Thus, polymers of adenylic acid (poly A) form quite stable dimers, with polyuridylic or polythymidylic acid (poly U, poly T) and a polymer composed of alternating A and T residues always tends to be double-stranded, held together by H bonds between opposite A and T residues. DNA was recognized by Watson and Crick as generally occurring in the stable double-stranded form and what was first an inspired hypothesis is now a well established fact: The two strands have complementary nucleotide sequences, so that opposite each A there is a T and opposite each G there is a C, and vice versa (*9*). These multiple and regularly spaced interactions lead to double-stranded helix formation, and the stacking of the bases which form shelves perpendicular to the axis of the helix, further stabilizes their linkage. The double-strandedness is not a necessary structural feature for biological function, since DNA occurs in single-stranded form in certain small viruses, and RNA generally occurs in single-stranded form only. Nevertheless, this affinity for the complementary base seems to be the directing force that usually ensures faultless replication of the long molecules of nucleic acids. Thus, the presence of a polynucleotide of certain base sequence leads to the formation of a complementary strand when nucleotides are being polymerized by enzymes *in vitro*. Features of the molecule other than the hydrogen bonding "surface" of the bases, such as the sugar (ribose or deoxyribose) or the methyl group in the 5 position (thymine or uracil) do not affect this principal feature of the replication process. It represented a major advance in molecular biology when Kornberg and later many other research groups began to study the reproduction of specific nucleotide sequences in cell-free systems, starting with either RNA or DNA as the template (*6, 10–12*). The energy necessary for the linking of one nucleotide to the other in such systems is supplied by using the energy-rich 5′-triphosphates of the four nucleotides, or deoxynucleotides, pyrophosphate being released from each condensing unit (Figure 3).

If we now return to consider the action of nitrous acid, it is obvious that each deamination of cytosine to uracil (C → U) will be replicated as such (U information being passed through A to U, instead of C → G → C). Deamination of A on the other hand yields a 6-oxypurine which resembles G more than A and thus might be replicated as such (A + HNO_2 → hypoxanthine ≅ G → C → G) although it might also lead to inactivation of the molecule. Finally, the deamination of G to xanthine does not appear mutagenic in terms of the H-bonding site of the purine, but may well be inactivating. Other modifications of nucleotides, such as the introduction of alkyl groups on the purines or of bromine atoms or hydroxylamine residues on the pyrimidines have been reported to cause occasional mutants. But all these reagents are of a low mutagenic efficiency, compared to nitrous acid acting on RNA. These infrequent mutations are probably the consequence of an occasional error in the replication of a base which is slightly deformed because it carries a substituent on its "back."

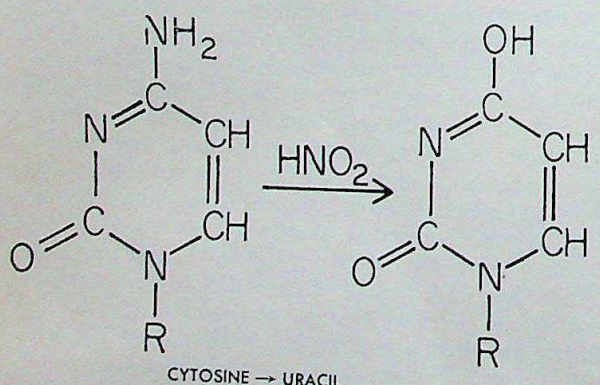


Figure 2. Deamination of the bases containing amino groups in RNA.

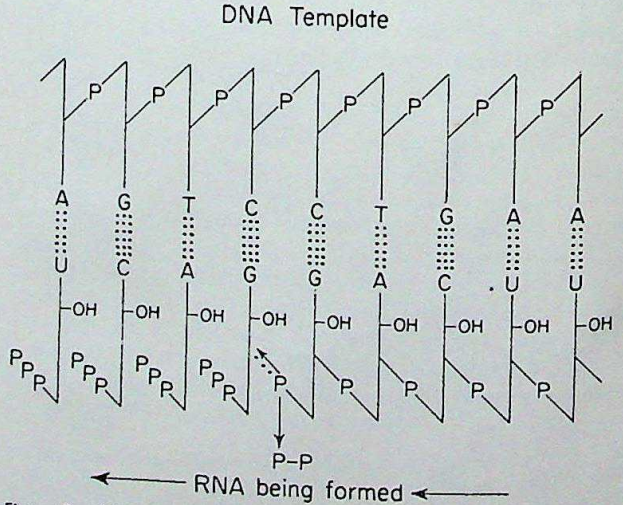


Figure 3. Schematic presentation of RNA formation on a DNA template. The vertical line represents the sugar; the letters, A,G,U,C,T, the bases; and P the phosphate group. The polymer chain is shown to form from right to left. The dotted lines represent H-bonds.

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Role of RNA in Protein Structure

This was a review in a nutshell of the recent advances made in our understanding of the chemical mechanism by which nucleic acids replicate and transmit their structure from DNA to RNA. However, the other critical aspect of nucleic acid function lies, as we stated earlier, in their ability to transmit this structural information to the enzyme proteins which control metabolism. Concerning this mechanism we knew very little until 1961. Even without knowledge of the mechanism, however, useful information concerning the interrelationship of proteins and nucleic acids was again derived from virus research. For each virus particle consists of both the genetic material and one of its phenotypic expressions: the protein that gives it its shape and stability. It was long known that the proteins of related strains of a virus could be very similar to one another, or that they could differ in specific manner. In the case of TMV the protein coat of each virus particle consists of 2130 identical protein molecules each composed of 158 amino acid residues. Methods for the analysis of the amino acid composition are now sufficiently exact to permit the detection of the presence of one amino acid more or less in such a unit. It thus has become evident that strains of TMV, be they naturally occurring or produced by one of the mutagenic reactions described above, may be identical in composition but may also differ one from another by one or several (up to 30) amino acid replacements (*13, 13a*). Replacement means that any decrease in one amino acid is always compensated by an increase in another so that the total number of 158 residues appears unchanged. The general belief that the amino acid composition is a genetically controlled feature of the virus was proven by us a few years ago when we started to disassemble and reassemble (reconstitute) virus particles. We then found that the strain origin of the nucleic acid alone determined the nature of the progeny particle, including its amino acid composition, even if the RNA was encased *in vitro*, through reconstitution, in protein from a different strain, greatly differing in composition (*14*) (Figure 4).

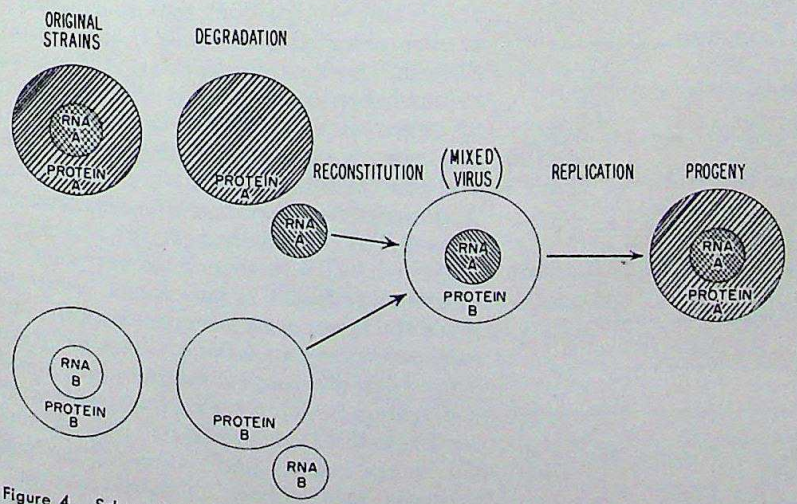


Figure 4. Schematic presentation of mixed reconstitution of the RNA of strain A with the protein of strain B of a virus. The progeny of such mixed virus shows all the properties, including protein composition, of strain A

We have since gone beyond composition. For now through the work of one research team at our laboratory, and another at Tübingen, the complete sequence of the 158 amino acid residues along the peptide chain is known (*15, 15a, 16*) (Figure 5). We can therefore ask and answer questions, such as: which particular serine is replaced by phenylalanine in this mutant? The virus protein fulfills an important function in protecting the viability of the virus, and certain amino acid replacements may interfere with this function. Thus, those virus strains which we are able to study have passed the screening test of natural selection, and are not grossly deficient in protein quality. Yet all strains appear more or less deficient in viability compared to the original common TMV, presumably because this is the strain best adapted to its environmental circumstances. In one specific instance we found this fact illustrated in clear fashion. The replacement of proline #156 (on the amino acid sequence map) by leucine in a strain resulting from nitrous acid treated RNA rendered that strain susceptible to extensive degradation by the enzyme carboxypeptidase (*13*). In the common strain the presence of proline in position 156 restricts enzymatic attack to the terminal threonine (#158) which may be jettisoned without detriment to the infectivity and stability of the virus. Thus, we have here observed that a change in RNA structure, presumably a replacement of C by U, leads to a change in protein structure which affects the stability of the viral coat protein, and thus presumably the viability of the virus (*13*).

Mechanism of Information Transfer from RNA to Protein

Studies of the type discussed above are supplying more data concerning amino acid replacements as a consequence of mutation. However, they tell us nothing about the mechanism of information transfer from the RNA to the protein. This so-called coding problem has been discussed in theoretical manner for a number of years. Since only 4 different nucleotides can code for 20 amino acids, they must act in consort, and only triplets of nucleotides give a sufficient number of permutations to suffice for the purpose (pairs of nucleotides would give $4^2 = 16$ symbols, while triplets give $4^3 = 64$ possible symbols). Recently, some experimental evidence was reported by Crick and coworkers in support of the triplet theory, but other possibilities have certainly not been ruled out (*17*). Regardless of this number, it appears probable that the base pairing principle accounts for the translation of sequence information from RNA to protein, as it does from DNA to RNA. This is possible because each amino acid is carried to the protein synthesizing components of a cell, the so-called ribosomes, by a specific transport RNA, to which it is bound by ester linkage to the ribose of a terminal adenosine. Thus a certain nucleotide sequence on the information-carrying DNA-derived RNA is believed to attract by base pairing a certain attaching site of the transport RNA and thereby to bring its amino acid near to that attaching at the

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neighboring site (*18*). These neighboring amino acid residues may then exchange the ester linkage holding them to their specific transport-RNA for the amide linkage which locks them into a peptide chain. Much of this process is still uncertain and difficult to envisage, but the principle features may be correct. Whatever the detailed mechanism, recent work by Nirenberg and Matthaei (*19*), and subsequent work by a team in Ochoa's laboratory (*23*) have definitely established means of studying this reaction.

The protein-making factory, the ribosomes, require energy supplied by ATP, as well as the twenty different amino acids as building blocks, each with its corresponding activating enzyme and transport RNA. If one, several, or all of the amino acids are radioactive, their incorporation into peptide and protein linkage can easily be detected and measured. Besides these components, the system needs instructions as to which protein to make. Such blueprints are usually supplied by the DNA of the cell, as transmitted via messenger RNA. If no DNA is present or if it is removed by means of the enzyme DNAase, the messenger cannot be replaced as it becomes used up, and the factory grinds to a halt. It was Nirenberg's discovery that the addition of various types of RNA to the system at that time resulted in a new spurt of production, as measured by amino acid incorporation (*16*). What was being produced? Obviously one would have to expect that it was the message carried by the added RNA which would be translated into protein structure. Yet, if one used the protein factory of a bacterium (*E. coli*), and if one added an RNA as strange to this system as that of a plant virus (TMV-RNA), the idea that TMV-protein would be synthesized would seem almost too fantastic to entertain. Fortunately, Nirenberg and Matthaei refused to reject this possibility and initiated joint studies with our laboratory to characterize the nature of the radioactive protein synthesized by their cell-free *E. coli* enzyme system under the direction of TMV-RNA.

The result of a variety of complex tests is as follows: A good part of the protein seems to resembles TMV protein, as shown by immunological tests, and by amino acid sequence studies. Yet, a definite chemical difference exists between the two proteins. The TMV-protein has a free amino group at one end of the peptide chain of the TMV-protein. Further, in regard to its function to form a coat for the viral RNA through aggregation of chains, the newly synthesized protein was definitely deficient. The presence of this protein actually interfered in specific manner with the aggregation of the normal protein. It appears quite possible that a comparatively minor chemical deficiency, such as the absence of the N-terminal acetyl group, might account for this behavior. The "incomplete" protein unit might fit and attach to its neighbors in the course of the helical stacking of "good" protein subunits but, lacking the proper configuration "on its back," the incompletely synthesized protein might thereby terminate the process of protein aggregation and resultant rod formation. Both the nature of the chemical and of the functional deficiency of the TMV protein synthesized in the cell-free *E. coli* system are under continuing investigation, and much remains to be learned about the mechanism of this reaction. However, the close relationship between TMV protein and the product of the enzymatic amino acid polymerization in *E. coli*, when directed by TMV-RNA, is suggested by serological, physicochemical, amino acid sequential, and functional tests, and thus appears to be a reality (*20*).

The potential implications of this finding, if confirmed, are great and manifold. First, it would give a distinct answer to the question of the universality of the code. If the genetic language of a plant virus RNA can be understood by a bacterial system, then it would appear probable that the code is the same or nearly the same for most if not all organisms. This conclusion is borne out by several other recent findings. Further, the concept of messenger RNA, as first proposed on quite different grounds by Monod and others (*21*), is supported and broadened by those findings. For the nature of the added RNA appears to be the principle agent that determines the nature of the protein produced by the synthesizing factory of *E. coli*. A viral RNA can act as messenger, and it does so most probably by serving as the template which assures the reproduction of all that pertains to the making of a virus. It seems now certain that the viral RNA encompasses more than the template for the coat protein, although this is the only product that was looked for in the reported biosynthetic experiments. Since RNA alone is infectious, it is logically evident that it must supply the template for its own replication, and for the production of any new enzymes required for the synthesis and the spreading of the virus and the appearance of its symptoms. The 6400 nucelotides of TMV-RNA are believed, on the basis of the triplet code theory, to carry enough information for 2130 amino acid sequences while the viral coat protein consists of chains only 158 amino acids long. The incorporation of histidine and methionine by the *E. coli* system is stimulated to the same extent by TMV-RNA and by HR-RNA, although the common TMV lacks these amino acids in its coat protein, but the HR-strain contains them (*14*, *20*). And finally we know that many mutants produced by chemical modi-

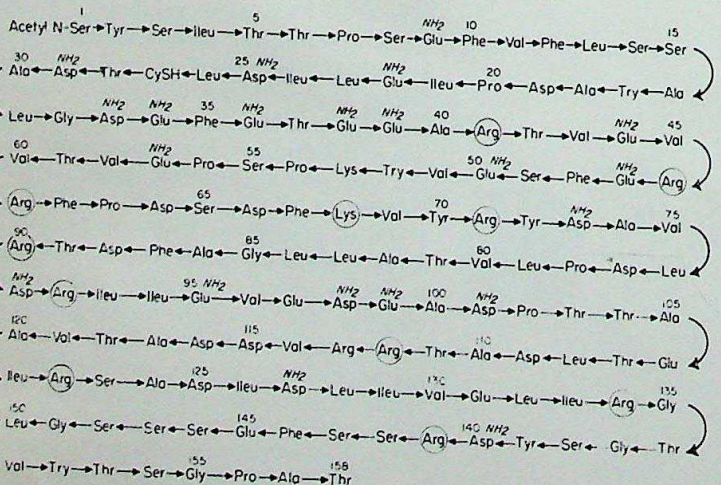


Figure 5. Sequence of the 158 amino acid residues in the protein subunit of tobacco mosaic virus (*15a*, *16*).

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fication of the RNA do not show any differences in their amino acid composition from common TMV from which they are clearly distinguishable by the symptoms they produce. Obviously, we must assume that chemical analysis should reveal differences in the RNA of these strains, but the methods of nucleotide analysis do not yet approach the precision necessary to find minimal changes such as the transformation of one or two out of 1200 cytosines to uracils.

As a consequence of these facts and considerations, our former oversimplified concept that TMV-RNA represents nothing but the nucleic acid equivalent of the TMV-coat protein had to be abandoned for the more complex one that it carries all kind of information, much of which we are not yet able to recognize. Thus, it is not surprising that the *E. coli* system as directed by TMV-RNA causes the synthesis of much protein which is not related to TMV-coat protein. As usual when a new mountain of scientific knowledge has been climbed it turns into a foothill compared to the range of peaks now exposed to view, all challenging further effort.

Another instance where the *E. coli*-protein making machinery was found to accept direction from a specific RNA, namely that of a coli-phage, has recently been reported. Be it due to the normally closer relationship of that RNA to the bacterial system, or just to luck, an appreciable fraction of the observed amino acid incorporation resulted in what seemed to be phage-coat protein. However, functional tests were not attempted in this instance (*22*).

The message carried by the viral RNA has turned out to be more complex than first bargained for. It was thus fortunate for Nirenberg and Matthaei, that soon after they initiated the study of this reaction, they sought and found a simpler messenger, an isolated peak of discovery which immediately revealed a wide new area for the rapid advance of knowledge. Since the work of Grunberg, Ortiz, and Ochoa (*23*), it had been possible to prepare polynucleotides by means of certain bacterial enzymes acting on nucleotide 5′ diphosphates. The polymer of uridylic acid alone (poly-U), as prepared in this manner, proved very active in stimulating the *E. coli* system to incorporate or polymerize one and only one amino acid, phenylalanine (*19*). The conclusion was soon firmly established that some number of uridylic acid residues, possibly 3, in polymer linkage coded for phenylalanine. This represented the first experimental breakthrough on this crucial front of scientific progress, the correlation of nucleotide with amino acid sequences. A systematic study of the effects of polymers prepared from pure di, tri, and tetranucleotides in this system will undoubtedly be performed and will give the definitive data on the code. Unable to await the results of this laborious process, workers at Ochoa's and Nirenberg's laboratory have studied the effects of random copolymers of 2 or 3 nucleotides, and have obtained data about the nucleotide composition, though not the sequence, of possible code symbols for all amino acids (*19*). This work will not be discussed in detail here, for it is the talk of the scientific community and is being reviewed by others. A number of scientists not engaged in the primary discoveries have brought their ingenuity to bear on the problem and have built new theoretical card houses concerning coding sequences, evolutionary developments, etc. These, too, will stand or fall with the laborious accumulation of data, so distasteful to those who feel pressed to join the band-wagon. The name of that vehicle is the Proceedings of the National Academy of Sciences, and it travels once a month, and one month's delay in publication might mean the loss of a man's right to claim 5 years later when the data are at hand, that he had first guessed at a particular conclusion.

Mutants and Coding

We will now return to our main topic of discussion, the viruses and what we can learn from them in regard to the mechanism of replication. As discussed earlier, the effect of mutation on the amino acid composition of the protein of TMV has long been the subject of intensive study in two laboratories. Many of the mutants were the result of nitrous acid treatment of the RNA, and could thus with some probability be attributed to a change of C → U. Obviously, these data represented a good test for the validity of the coding symbols derived from the *E. coli* work of Nirenberg's and Ochoa's laboratory. The first observation that phenylalanine is coded by poly-U alone means that deamination (C → U) may lead to the replacement of other amino acids by phenylalanine, but never to the reverse process. In accord with this, serine was found replaced by phenylalanine in several strains, while phenylalanine has not been found replaced by other amino acids (*13*, *13a*). The frequent changes involving proline, the code symbol of which is rich in C, are also in accord with expectation. In general, it can be stated that the majority, but not all, of the observed amino acid exchanges are in accord with the code symbols proposed for these amino acids, on the basis of C → U transformations. A few of the others can be accounted for by the hypothesis that A, deaminated to hypoxanthin resembles and codes like G. Others that do not fit could signify erroneous coding symbols, but probably they are indicative of a strain which resulted from spontaneous mutation (or contamination) rather than being evoked by the deamination reaction. Since each strain is the progeny of a single infective molecule, these unfortunately are definite and ever-present possibilities. Seen as a whole, the agreement between the two sets of data, each weighted by its own errors and uncertainties, is as good as might be expected, and lends further support to the validity and to the universality of the code symbols as elucidated with *E. coli*, and tested against tobacco mosaic virus. Other systems using bacterial or bacteriophage strains promise to supply similar and possibly more incontrovertible evidence along such lines.

Conclusions

Let us now review the subject of this article. We have discussed the chemical nature of the nucleic acids, both RNA and DNA, which are the carriers of genetic and possibly also of other types of information in all organisms. We have considered methods by which this information can be changed through chemical modification, and how this process may result in mutation. We have described mechanisms by which genetic

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information can be transferred from one type of nucleic acid to another, and from nucleic acid to protein. This was illustrated most convincingly with the bacterial protein synthesizing system. Thus, a mixture of enzymes and ribosomes derived from *E. coli* makes the protein which it is directed to make by an added RNA, the so-called messenger RNA, whether this RNA is as complex as that of a virus or as simple as polyuridylic acid. We have briefly touched upon the enormous advances made in the past year in the elucidation of the code relating each amino acid to a corresponding nucleotide combination; and we have discussed the extent of agreement of these code symbols with amino acid exchange data observed in mutants of TMV and presumably due to specific nucleotide exchanges in its RNA. While this is the first mention of tobacco mosaic virus in this summary, most of the work and most of the discussion actually dealt with this virus, a fact which illustrates the versatility and general usefulness of viruses as study objects in research on the fundamental principles of molecular biology.[1]

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[1] A review of this subject matter for the layman or beginning student of molecular biology is available in form of a small paper back, "Design and Function at the Threshold of Life: The Viruses," by H. Fraenkel-Conrat, Academic Press, New York 1962.

CACT Fifth Summer Conference

August 18–24, 1963

The California Association of Chemistry Teachers, with the cooperation of Occidental College and the support of California firms, local ACS sections, and the National Science Foundation, is planning its Fifth Summer Conference.

Program. Sessions will open with an address by Dr. Glenn S. Dumke, Chancellor of the California State Colleges. Lectures by nationally prominent authorities in several fields of chemistry including instrumental analysis (H. V. Malmstedt, Illinois), structural organic (M. S. Newman, Ohio State), physical (E. C. Lingafelter, Washington), and inorganic chemistry (H. Hynam, Argonne, and H. D. Kaesz, UCLA). Presentations will be at the college level rather than that of the university specialist. Afternoon roundtables will include discussions of newer ideas in laboratory instruction in high school (CBA and CHEM) as well as college organic and physical chemistry. Dr. Karl Folkers, retiring ACS president, will be the speaker Saturday. His topic will be "Research Trails to New Therapy."

Participants. College and high school teachers.

Date. Sunday evening, August 18, through Saturday noon, August 24.

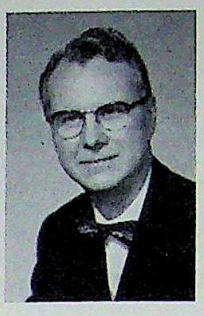
Location. Asilomar Beach State Park, Pacific Grove, California—on the famed Monterey peninsula adjacent to Monterey (United Airlines service) and Carmel; forty miles from Big Sur.

Cost. Average below $70 for the period, depending on accommodations. Excellent housing and food.

For Information Write. Mrs. Wallace A. Craig, CACT Conference coordinator, 1199 Laurel Street, Pasadena; or Dr. Frank L. Jones, Jr., Occidental College, Los Angeles.

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. . . from the CHAIRMAN

EDWARD C. FULLER

Objectives and Needs

For more than forty years the members and officers of the Division of Chemical Education have striven for the improvement of chemistry teaching. The decades since 1921 when Edgar F. Smith of the University of Pennsylvania was the first chairman of the Division have witnessed tremendous growth in our science. This rapid expansion in knowledge has necessitated fundamental changes in our ways of teaching chemistry, as pointed out by John C. Bailar, Jr.[1] Discoveries of new facts modify old theories or lead to new ones, presenting both the teacher and the student with a fascinating and stimulating—but sometimes bewildering—array of material to be mastered.

Chemistry Teaching at All Levels Is Interrelated. In this time of rapid growth and change, we who teach chemistry must be concerned not only with our own pedagogical problems but also with the advance of chemical education on all fronts. The college teacher must know what university teachers expect in the preparation of students for graduate study. The university teacher must be aware of the limitations which prevent the undergraduate college from fulfilling the desired role completely and must provide various means for the first year graduate student to consolidate his preparation for doctoral candidacy.

The teacher of first-year college chemistry must build on the chemical knowledge brought by his students from their secondary school studies of chemistry or he will lose the interest and enthusiasm of the better students. The high school chemistry teacher cannot be of maximum effectiveness unless he knows what science his pupils have had in junior high school, and the teacher in junior high must know about the science taught in the elementary school.

The chemistry teacher in the junior college cannot plan or teach an effective two-year sequence of chemistry courses unless he knows what his students have done in high school and what will be expected of them if they transfer to a four-year college in pursuit of a bachelor's degree. He needs also to know what technological roles the graduates of his college can fulfill—and how they can be most effectively trained for these.

The basic objectives of the doctoral program in the graduate school need to be understood by the university teachers who direct the program as well as the college, industrial, and governmental officers who utilize the services of graduates with the PhD. The role of the man with a master's degree in meeting the ever widening demands for scientifically trained people in education, government, and industry needs to be studied along with plans for making the degree of greater worth. The college teacher needs to know what the employers—school administrators, industrial chemists, directors of government laboratories—expect of the man with the bachelor's degree.

The reflective teacher of chemistry realizes that, indeed, "no man is an island" and that his own professional effectiveness is inextricably bound up with the work of his fellow teachers in other universities, colleges, and schools. It is precisely this interdependence which makes the role of the Division of Chemical Education so important. If a chemist is to grow in stature as a teacher, he needs to know what other teachers are doing (as noted by Harry F. Lewis[2]), to expand his knowledge of chemistry continually (as pointed out by Arthur F. Scott[3]), and to develop his skills in presenting chemistry to his students. All three of these needs are being met by various activities carried on by the Division through its officers, committees, and members.

What the Division Does. The activities of the Division may be summarized under three main headings: (1) stimulating the writing of scholarly papers dealing with new ways of correlating and presenting chemical knowledge, new ways of teaching in the classroom and laboratory, and the philosophy and principles which underlie chemical education; (2) providing teachers with opportunities for the oral exchange of ideas and experiences; (3) offering services to chemistry teachers which will enhance their value to the profession and to society.

Stimulating the Writing of Scholarly Papers. The writing and presentation of papers are encouraged by programs at the semiannual national meetings of the American Chemical Society which are planned by the Program Committee of the Division. The accessibility of an even larger audience through the Division's JOURNAL OF CHEMICAL EDUCATION with its 16,500 subscribers offers further inducement to the writing of such papers. All of us who subscribe to the JOURNAL have a "living textbook" which does much to keep us abreast of new developments in our field—and at a price to us which is but a fraction of the cost of publication. As we look through the pages of advertising which finance a major portion of these costs, let's not forget to express our interest now and then in the products we see presented there. A word of inquiry—noting that it was stimulated by reading an ad in the JOURNAL—will do much to make our advertisers feel it's worthwhile to continue their heavy subsidy of our publication. The fact that authors who write for our JOURNAL do not have to pay a publication charge (as is the case for many chemical journals) contributes to the effectiveness of the periodical for disseminating scholarly ideas.

Opportunities for Oral Exchange of Ideas. Many papers are presented first at national meetings of the Division and are then published in the JOURNAL. The Program Committee of the Division not only arranges sessions for the presentation of general papers but also plans symposia on special topics. These symposia have been heavily attended. They have dealt with such widely diversified topics as the chemistry of fused salts, institutes and conferences, audio-visual aids, solid state chemistry, training of literature chemists, sponsored research, radiation chemistry, theories of chemical bonding, honors programs, recent advances in analytical, physical, and inorganic chemistry, and the teaching of organic and inorganic, thermodynamics, colloids, and biochemistry. One needs only to look at the articles in any issue of the JOURNAL OF CHEMICAL EDUCATION to realize how varied is the intellectual fare of the Division at national meetings.

Though we may exchange information and opinions with our colleagues at national meetings, more extensive opportunities are provided in institutes and conferences. Some of the most significant and fruitful work accomplished by the Division has been

[1] J. CHEM. EDUC., 38, 434 (1961).

[2] J. CHEM. EDUC., 36, 432 (1959).

[3] J. CHEM. EDUC., 37, 442 (1960).

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the promoting and sponsoring of these gatherings, where a teacher may spend two to ten weeks studying intensively a particular phase of chemistry or ranging widely over a number of topics. Such meetings provide unparalleled opportunities for learning both new chemistry and new techniques for teaching it. Increased numbers of these are needed, especially for college teachers, now that the new CBA and CHEMS courses for high schools—which grew out of activities sponsored by the Division—are being presented at so many institutes. Institutes and conferences dealing with problems of mutual interest to secondary school and college teachers and open to participants of both kinds have been particularly fruitful.

Services to Teachers. In addition to stimulating written and oral discussions of chemistry and chemistry teaching, the Division of Chemical Education provides important services to teachers. Of major magnitude among these is the work of the Committee on Examinations. Literally scores of active chemistry teachers work on the preparation of examinations under the leadership of twenty-three members of the Committee. Twenty-seven tests—19 for college, 5 for secondary school, 3 for graduate school—are now available. About 300,000 college and high school students in about 900 colleges and 1000 high schools are taking these tests this year. Three new tests were produced last year, and new tests for all courses and at all levels are in preparation. The Committee's work is taking on an international flavor with a number of sales in foreign countries and translations of tests into Japanese, Indonesian, Portuguese, and Spanish. Some foreign universities have inquired about using the graduate level tests. The University of South Florida has been most generous in making space and technical services available to the Committee free of charge.

Another service to teachers is the program of Visiting Scientists in Chemistry arranged by a committee of this Division. In 1961–62, 140 college visits were made by 75 visitors and 170 high school visits by 41 visitors. Seven visitors from foreign countries lectured at 54 universities. More of each kind of visit are being planned by the committee for 1962–63.

A third form of service rendered to teachers involves the design and trial of new laboratory experiments and lecture demonstrations and the improvement of more traditional ones. Several members of the Division are working along these lines on committees which will ultimately publish their results in the JOURNAL OF CHEMICAL EDUCATION or some other appropriate medium.

Collecting and supplying information of special interest to chemistry teachers has been another activity of various committees of the Division. Listing opportunities for graduate work in chemistry open to secondary school teachers, analyses of programed instruction, and preparation of a list of books most needed for a junior college chemistry library are representative of this kind of information gathered and disseminated by members of Divisional committees.

The Goals and Philosophy of Chemical Education. Discussion of goals and philosophy almost always arises when members of the Division are gathered together—in committee meetings, in technical sessions, or at institutes and conferences—to consider almost any problem in chemical education. Divisional committees are studying various aspects of curriculum, aids to the teacher, physical facilities for instruction, and cooperation with other groups interested in chemical education. Several studies now in progress cover the front from elementary school through the junior college and the four-year college.

How the Division Works. The officers and committee chairmen for 1963 are listed at the end of this report. The duties of the officers are those usually associated with their positions. The life-blood of the Division is the activity of its committees. When they are productive, the Division as a whole flourishes; when they are sluggish, the Division languishes. The productive activities of the committees on Program, on Examinations, and on Visiting Scientists have already been described. The JOURNAL OF CHEMICAL EDUCATION continues its record of excellent publications under the editorship of W. F. Kieffer and with the guidance of the Division's Board of Publications.

The other three committees were established in 1963, replacing the Committee on Institutes and Conferences and the Committee on Teaching. The principal purpose of the Committee on Curriculum is to study the needs for curricular revision, including such matters as course content, sequence of courses, and the philosophy of chemical education. The committee is concerned with the chemistry taught at all levels from the elementary school through the four-year college. The Committee on the Teacher and His Work is set up to aid the teacher at any level of instruction in doing a better job. This may include stimulating proposals for institutes and conferences, encouraging the production of monographs and films, promoting programs recognizing the excellence of teachers, improving teacher education, studying library and laboratory needs of teachers of chemistry at various levels, evaluating criteria for measuring teaching loads, etc. The principal purpose of the Committee on Relations with Government Agencies, Industry, Foundations, and Professional Societies is to serve as a clearing-house of information concerning activities in chemical education carried out by agencies other than the Division. We wish to supplement—not duplicate—the work of these groups.

The Division of Chemical Education Needs You. Though many members of our Division are working hard on various problems in chemical education, much needs to be done which cannot be accomplished because of a shortage of manpower. Your interest as a reader of THIS JOURNAL indicates your concern for improving chemical education. *The Division needs you*—and you can help in several ways. (1) Become a member if you are not already enrolled; write to W. G. Kessel about this. (2) Write to the chairman of the Division or to any of the committee chairmen, telling them about problems in chemical education you would like to see the Division attack. (3) Let the chairmen know if you are willing to spend some time working toward the solution of these problems. (4) Tell your colleagues in chemical education about the work of the Division and urge them to join us. *Will you help?*

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Chem Ed

LETTERS

To the Editor:

In "Textbook Errors, 40" (J. CHEM. EDUC., *39*, 527 (1962)), D. W. Rogers discusses the derivation of the Gibbs-Duhem equation and asserts that it is "not correct" to integrate the equation

$$dG = \bar{G}_1 dn_1 + \bar{G}_2 dn_2 \qquad (1)$$

so as to obtain the equation

$$G = \bar{G}_1 n_1 + \bar{G}_2 n_2 \qquad (2)$$

I should like to point out that his assertion is not correct.

In equations (1) and (2), G is an extensive thermodynamic property of a mixture, $\bar{G}_1$ and $\bar{G}_2$ are partial molal quantities of components 1 and 2, and n_1 and n_2 are the *number of moles* of components 1 and 2, respectively. Now partial molal quantities are intensive properties and are independent of any actual values of n_1 and n_2, but do depend on the composition of the mixture, that is, upon the ratio n_1/n_2. It is to be understood that n_1/n_2 is constant during the integration of equation (1).

Lewis and Randall put it this way ("Thermodynamics," McGraw-Hill Book Co., Inc., New York, 1923, p. 42):

> If, therefore, to a given solution we add the several constituents simultaneously, keeping their ratios constant, these partial molal quantities will remain constant. We may therefore integrate equation (1), keeping n_1, n_2, . . . in constant proportions, and find equation (2)."

Also Rogers' equation (1) would not be correct for a system of more than two components.

F. E. CONDON

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EDITOR'S NOTE: This and the following pages present only a part of the correspondence generated by the article which appeared in October as "Textbook Errors, 40." We apologize to the authors of letters other than those appearing, notably Professor S. D. Christian of Oklahoma, who stressed essentially the same points as those made here. The published letters have been abbreviated in the interest of saving space. Readers should blame any abruptness or seeming lack of transitions on the editor's blue pencil, not on the correspondent's lack of style.

Since $\bar{G}_1$ and $\bar{G}_2$ are intensive, under the conditions stated previous to equation (1), i.e., $G = f(n_1, n_2)$, they are functions only of n_1/n_2 and must be constant if n_1/n_2 is constant. As the paper shows, this leads to a trivial result for the Gibbs-Duhem equation,

$$n_1 d\bar{G}_1 + n_2 d\bar{G}_2 = 0$$

The significance of the Gibbs-Duhem equation is not that $n_1 d\bar{G}_1$ and $n_2 d\bar{G}_2$ are zero which, in general, they are not, but that they are equal and opposite.

Further reflection shows that the "simple proof" of Euler's theorem given by Mellor is itself not general but can easily be extended to cover the present case.

Consider equation (6)

$$G = \Sigma\, a\, n_1^{\alpha} n_2^{\beta}$$

If α and β can only be zero or one and the sum of α and β must be one for a first degree homogeneous function,

$$G = a_1 n_1 + a_2 n_2$$

and we see the identity between a_1, a_2 and $\bar{G}_1$, $\bar{G}_2$ respectively. For the differentiation shown

$$\frac{\partial G}{\partial n_1} = \Sigma a\alpha n_1^{\alpha-1} n_2^{\beta}$$

and

$$\frac{\partial G}{\partial n_2} = \Sigma\, a\beta n_1^{\alpha} n_2^{\beta-1}$$

a must not be a function of n_1 or n_2.

Since we are *not* willing to allow a to be constant we must show that an identical result to my equation (7) is obtained when a is taken to be a function of n_1/n_2. Differentiating equation (6) under the condition that n_1/n_2 is *not constant*

$$\frac{\partial G}{\partial n_1} = \Sigma a\alpha n_1^{\alpha-1} n_2^{\beta} + \sum \frac{\partial a}{\partial\left(\frac{n_1}{n_2}\right)} \left(\frac{1}{n_2}\right) n_1^{\alpha} n_2^{\beta}$$

and

$$\frac{\partial G}{\partial n_2} = \Sigma a\beta n_1^{\alpha} n_2^{\beta-1} + \sum \frac{\partial a}{\partial\left(\frac{n_1}{n_2}\right)} \left(\frac{-n_1}{n_2^2}\right) n_1^{\alpha} n_2^{\beta}$$

Upon multiplying $(\partial G/\partial n_1)$ by n_1 and $(\partial G/\partial n_2)$ by n_2 and adding their products, the second and fourth terms drop out and the identity is proven.

The second criticism is, "Equation (1) would not be correct for a system of more than two components." Please note the sentence before equation (1) which begins, "For simplicity, the equation will be worked out for a system of two composition variables, $G = f(n_1, n_2)$". . . .

The continuation of the same sentence ". . . that is, T, P, n_3, n_4 . . . n_n are constant." leads to a digression which may be worth mentioning. If n_3, n_4 . . . n_n are zero, the system is binary and equation 1 holds. If n_3, n_4 . . . n_n are not zero, but constant, equation 1 still holds because it refers to an *infinitesimal* change in n_1 and n_2. If there is finite change in n_1 and n_2 which takes place in a finite system (not infinitely large) then the ratios of n_3, n_4 . . . n_n to the total number of moles

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change and we may not apply Euler's equation for a total differential.

I apologize for the omission of a comma in equation (5) and a superscript α in the derivative below equation (6) in the original paper.

D. W. ROGERS

ROBERT COLLEGE
ISTANBUL, TURKEY

To the Editor:

It was with great interest that I read the symposium on the "Teaching of Thermodynamics" in the October, 1962 issue. I look forward to reading future symposia of this type.

In the same issue there appeared a most interesting discussion of the Gibbs-Duhem equation (THIS JOURNAL, **39,** 527 (1962)) (in its most general form as applied to any extensive function of composition at constant pressure and temperature). Prof. Rogers in discussing this in terms of textbook errors is really writing about errors of omission rather than errors of commission.

In writing my book on thermodynamics (*3*), I was faced with the problem of whether to use the approach of Gibbs in deriving this equation or the more rigorous method of MacDougall (*5*) employing the elegant applications of Euler's theorem on homogeneous functions. As pointed out by Prof. Bent (THIS JOURNAL, **39,** 491 (1962)) in the very first article of the above-mentioned symposium, Gibbs had the genius of circumventing mathematical difficulties. Because Euler did his work over a century before Gibbs, it is doubtful that Gibbs was not aware of Euler's theorem, yet he chose to avoid the abstract mathematical approach and adhere to a physical interpretation. Being a concise and sophisticated writer, Gibbs' derivation (*1*) is so simple that it usually escapes comprehension at the first reading (it took me at least ten readings to fully appreciate his approach).

I therefore chose to use Gibbs' method, but where Gibbs used one sentence, I ended up with several paragraphs. His concept of "integration through the mass" not only gives us an extremely simple approach to the derivation of the Gibbs equation of existence for homogeneous substances in equilibrium (Gibbs-Duhem equation) but later serves as a basis for deriving his equations for stable phase conditions (*2*).

It is my feeling that the Euler theorem should not be introduced until the student has obtained a full understanding of the physical concepts (either in graduate work or advanced undergraduate work for exceptional students). In fact, the Lewis and Randall (*4*) approach of deriving the Euler equation for extensive functions of state without the use of calculus should be introduced at an early level in the teaching of chemistry.

Prof. Rogers cites the clever use of a power series polynominal in the derivation of Euler's theorem by Mellor. A simple derivation suggested by Prof. F. H. Miller in his book on the calculus (*7*) which avoids this limitation may be given as follows:

If $$G(Zn_1, Zn_2) = Z^q G(n_1, n_2) \quad (1)$$

then G is homogeneous of degree q in n_1 and n_2.

Let

$$F = G(Zn_1, Zn_2) = F(Z, n_1, n_2)$$

and

$$G = G(n_1, n_2) \quad (2)$$

Combining (1) and (2)

$$F = Z^q G \quad (3)$$

Partial differentiation of (3) with respect to Z

$$\frac{\partial F}{\partial Z} = qZ^{q-1}G \quad (4)$$

Let $m_1 = Zn_1$ and $m_2 = Zn_2$, then

$$\frac{\partial m_1}{\partial Z} = n_1$$

and

$$\frac{\partial m_2}{\partial Z} = n_2 \quad (5)$$

By the calculus, since $F = G(m_1, m_2)$

$$\frac{\partial F}{\partial Z} = \frac{\partial F}{\partial m_1}\frac{\partial m_1}{\partial Z} + \frac{\partial F}{\partial m_2}\frac{\partial m_2}{\partial Z} = n_1\frac{\partial F}{\partial m_1} + n_2\frac{\partial F}{\partial m_2} \quad (6)$$

Combining (4) and (6):

$$n_1\frac{\partial F}{\partial m_1} + n_2\frac{\partial F}{\partial m_2} = qZ^{q-1}G \quad (7)$$

Let $Z = 1$, then $F = G$, $m_1 = n_1$ and $m_2 = n_2$ (8)

Combining (7) and (8)

$$n_1\frac{\partial G}{\partial n_1} + n_2\frac{\partial G}{\partial n_2} = qG \quad (9)$$

(which is Euler's theorem for two variables).

Let $\bar{G}_1 = (\partial G/\partial n_1)$ and $\bar{G}_2 = (\partial G/\partial n_2)$ then partial differentiation of (9) yields

$$n_1\frac{\partial \bar{G}_1}{\partial n_1} + \bar{G}_1 + n_2\frac{\partial \bar{G}_2}{\partial n_1} = q\bar{G}_1 \quad (10)$$

Since G is a continuous function:

$$\frac{\partial \bar{G}_2}{\partial n_1} = \frac{\partial^2 G}{\partial n_1 \partial n_2} = \frac{\partial^2 G}{\partial n_2 \partial n_1} = \frac{\partial \bar{G}_1}{\partial n_2} \quad (11)$$

Combining (10) and (11)

$$n_1\frac{\partial \bar{G}_1}{\partial n_1} + n_2\frac{\partial \bar{G}_1}{\partial n_2} = (q-1)\bar{G}_1 \quad (12)$$

and similarly for $\bar{G}_2$. Therefore, $\bar{G}_1$ and $\bar{G}_2$ are homogeneous of degree $(q-1)$. For $q = 1$ from (9)

$$n_1\bar{G}_1 + n_2\bar{G}_2 = G \quad (13)$$

where

$$G(Zn_1, Zn_2) = ZG(n_1, n_2)$$

from (12)

$$n_1\frac{\partial \bar{G}_1}{\partial n_1} + n_2\frac{\partial \bar{G}_1}{\partial n_2} = 0 \quad (14)$$

where

$$\bar{G}_1(Zn_1, Zn_2) = \bar{G}_1(n_1, n_2)$$

That is, G is homogeneous of degree 1 and $\bar{G}_1$ is homogeneous of degree 0. This is another way of saying that

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G is proportional to mass at constant composition (extensive) and $\bar{G}_1$ is independent of mass at constant composition being dependent on composition only (intensive). By combining (11) and (14), MacDougall (*6*) derives the generalized Gibbs-Duhem equation in an alternate manner.

ROGER GILMONT

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(1) GIBBS, J. W., "The Collected Works of J. Willard Gibbs." Vol. 1, Yale University Press, New Haven, Conn., **1948**, p. 87.
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(4) LEWIS, G. N., AND RANDALL, M., "Thermodynamics," McGraw-Hill Book Co., Inc., New York, N. Y., **1923**, p. 42.
(5) MACDOUGALL, F. H., "Thermodynamics and Chemistry," John Wiley and Sons, Inc., New York, N. Y., **1939**, p. 25–26.
(6) MACDOUGALL, F. H., *ibid.*, p. 28.
(7) MILLER, F. H., "Calculus," John Wiley and Sons, Inc., New York, N. Y., **1946**, p. 153 exercise 27.

To the Editor:

The total differential of any function f of r variables $(x_1, \ldots, x_r)$ is

$$df = \sum_i f_i dx_i \qquad (1)$$

where

$$f_i \equiv (\partial f/\partial x_i)_{x_j \neq i}$$

Suppose that f is homogeneous of the first degree in the r variables. The first partial derivatives of f are thus homogeneous of degree zero in the variables. Because of this fact, equation (1) can be integrated easily. The integration process consists of increasing all x_i from zero to x_i in such a way that the *relative* values of the variables are kept constant. Under this condition, f will increase montonically from $f(0, \ldots, 0) = 0$ to $f(x_1, \ldots, x_r)$, and all f_i's will remain fixed. The fractional change in x_i

$$dx_i/x_i = d\alpha \qquad (2)$$

will be the same, then, for all variables. Hence,

$$f(x_i, \ldots x_r) = \int \sum_i f_i dx_i = \sum_i f_i x_i \int_0^1 d\alpha = \sum_i f_i x_i \qquad (3)$$

which is Euler's theorem for a function which is homogeneous of degree one in $(x_1, \ldots, x_r)$. Equation (3) does *not* imply that the first partial derivatives of f must be held constant for any subsequent general variation in f. It is simply the result of a straightforward and rigorous integration which takes proper account of the degree of homogeneity of f and its derivatives.

The above method is essentially that used by Guggenheim[1] and by Gibbs.[2] Admittedly, all texts do not present this method in a satisfactory form, but such presentations are reflections upon the texts, and not upon the method.

The proof of Euler's theorem given above may be extended to functions which are homogeneous of positive integral degree. If the degree of homogeneity is two, equation (1) still holds, but the f_i's are now homogeneous of degree one. Hence, using (3),

$$f_i = \sum_j (\partial f_i/\partial x_j) x_j \qquad (4)$$

Introduction of (4) into (1) gives

$$df = \sum_{i,j} (\partial f_i/\partial x_j) x_i dx_i$$

$$= \frac{1}{2} \sum_{i,j} (\partial f_i/\partial x_j) d(x_i x_j) \qquad (5)$$

This may be integrated as before, since the second partial derivatives $\partial f_i/\partial x_j$ are homogeneous of degree zero. The result is

$$f(x_1, \ldots, x_r) = {}^1/_2 \sum_{i,j} (\partial f_i/\partial x_j) x_i x_j$$

$$= {}^1/_2 \sum_i f_i x_i \qquad (6)$$

using (4). Equation (6) is, of course, Euler's theorem for a function which is homogeneous of degree two in $(x_1, \ldots, x_r)$. Extension of the proof to higher positive integral degrees of homogeneity is obvious, but tedious algebraically. For functions which are homogeneous of degree zero, of negative integral degree or of positive or negative non-integral degree, the above method of proof cannot be used. While the method thus lacks generality, it does provide thorough insight into the meaning of homogeneity.

J. W. LORIMER

UNIVERSITY OF WESTERN ONTARIO
LONDON, ONTARIO

[1] GUGGENHEIM, E. A., "Thermodynamics," 4th ed., North-Holland Publishing Company, Amsterdam, 1959, p. 30.
[2] GIBBS, J. W., "Collected Works," Vol. 1, Longmans, Green and Co., New York, 1928, p. 87.

To the Editor:

. . . In Gibbs' method, the additivity equation for the extensive property G of a phase,

$$G = \sum \bar{G}_i n_i \qquad (1)$$

which gives the value of G for specified values of T, P and the n_i, is obtained by integrating the expression for the total differential:

$$dG = (\partial G/\partial T) dT + (\partial G/\partial P) dP + \sum \bar{G}_i dn_i \qquad (2)$$

The path of integration is chosen conveniently to be one of constant T, P and composition, because then the first two terms on the right vanish and the $\bar{G}_i$ are constant. As is often stated, this amounts physically to building up a finite quantity of the phase of given

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composition at given T and P by adding together small increments of the phase at the given T and P.

Now G is (assumed to be) a state function, single-valued in T, P and the n_i. Therefore the result expressed by equation (1) should be independent of the path of integration of equation (2). Equation (1) can then be differentiated in any manner desired, including with respect to variable $\bar{G}_i$, and there is no contradiction, because the integration of (2) has no bearing on the differentiation of (1). This is the point which seems to have been overlooked.

In order to get an expression for dG from (1) comparable with that in (2), we must differentiate (1) "generally," that is, with respect to the same variables as in (2), expressed explicitly or implicitly. These are T, P, and composition (upon which the $\bar{G}_i$ depend), and the mole numbers. This gives

$$dG = \Sigma\, \bar{G}_i dn_i + \Sigma\, n_i d\bar{G}_i \qquad (3)$$

There are thus two (general) expressions for dG, both of which are correct. This can only be the case if

$$(\partial G/\partial T)dT + (\partial G/\partial P)dP - \Sigma n_i d\bar{G}_i = 0 \qquad (4)$$

which is the Gibbs-Duhem equation.

Euler's theorem provides an alternative method of derivation, but we question its use at the second- or third-year level. Regardless of this, we object to a presentation implying Gibbs' method to be a "Textbook Error." We subscribe to a paraphrasing of a common expression: "There may be fibs from *other* nibs, but there ain't no fibs from Gibbs."

R. W. Missen and I. H. Spinner

University of Toronto
Toronto, Canada

To the Editor:

Missen and Spinner are correct in their assertion that $\bar{G}_i$ may be held constant in one step of the derivation of the Gibbs-Duhem equation and varied in the next if one assumes that the line integrals of $\bar{G}_i dn_i$ are independent of the path.

Taylor[1] derives this property of exact differential forms in two variables using Green's theorem which demands, among other things, that $\bar{G}_1$ and $\bar{G}_2$ be continuous and have continuous first partial derivatives over the closed region bounded by the line integrals in question. These assumptions are by no means obvious. Moreover, neither independence of the path nor the assumptions on which it depends are mentioned in relation to the Gibbs-Duhem equation in any of the textbooks which I cited to the column editor.

I have written neither to question the validity of the Gibbs-Duhem equation nor in criticism of J. W. Gibbs but rather in criticism of the unqualified use of one of his derivations in some books. It is pedagogically simpler and mathematically more rigorous (at least it involves fewer assumptions) to derive the Gibbs-Duhem equation from Euler's theorem than it is to derive it from the properties of exact differential forms. Also, the extension of Euler's theorem to functions of n variables is obvious, while the same could hardly be said of line integrals and Green's theorem extended to n^- space.

Donald W. Rogers

Robert College
Istanbul, Turkey

To the Editor:

Sister Agnes Ann Green of Immaculate Heart College has sent me a list of publications from that institution which I missed in my tabulations for the article "Maintaining and Sustaining Chemical Publications in Liberal Arts Colleges" [This Journal, **39**, 585 (1962)]. Dean Vernon L. Bollman has informed me that the PhD degree given by his institution, as recorded in the College Blue Book, is limited to the field of comparative literature, thus giving Occidental College liberal arts status by the criteria which I used. The data on publications abstracted in *CA* for these institutions is provided here. I suggest that readers add this to the previously published table. I regret any embarrassment the omissions may have caused the staffs and friends of these colleges. Errors in tabulation involving over one million abstracts can only be detected by direct communication with the parties involved.

John R. Sampey

Furman University
Greenville, South Carolina

Liberal Arts Colleges with the Most Consistent Record of Publications in *CA* for 1952–61.

Institution	'52	'53	'54	'55	'56	'57	'58	'59	'60	'61	Totals
Immaculate Heart	...	2	3	2	1	1	...	1	3	...	13
Occidental	...	1	1	...	..	1	2	1	...	3	9

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To the Editor:

The conclusion reached by Racusen[1] in his recent article on paper chromatography is one which has no foundation at the present time. There is no indication that we can "expect that some day we may have a system of organic analysis based entirely on paper chromatography . . . containing very exact relationships regarding structure and migration rate." Chromatography is at present very popular and has achieved many important results, but it has several limitations which should be realized by all chemists, especially teachers of chemistry.

The principal use of all differential migration methods (including paper chromatography) is for the separation of mixtures. Besides this, chromatographic sequences (R values) *partially* describe or characterize substances; they provide clues to the kind, location, and number of functional groups present in organic substances.

Many reports can be found in the literature of attempts to relate molecular structure and chromatographic behavior.[2] No simple relationship has ever been found. In fact, there is such great variation in sorbability with solvent, sorbent, solute (concentration and molecular structure), and temperature, that a widely applicable generalization will likely never be found.[3] Chromatographic data is useful in addition to decisive, conventional, chemical methods for determining composition and structure. Migration data alone cannot reveal composition, structure, or functional groups.[4] Only if pure reference substances are available for comparison of migration behavior can an unknown be identified chromatographically. The following quotation taken from a recent review emphasizes this alternative view:[5]

> There is a limited systematic basis for deriving the molecular structure from differential migration behavior. Highly selective with respect to separations, the methods are non-specific with respect to structure.

The enormous variation in chromatographic systems is further demonstrated by the fact that no useful theory has ever been developed for the prediction of the conditions required to perform a given separation. The chromatographer must rely on intuition, analogy, empiricism, and trial-and-error; I see no indication that any of this is about to change.

JOSEPH SHERMA

LAFAYETTE COLLEGE
EASTON, PENNSYLVANIA

[1] RACUSEN, D., J. CHEM. EDUC., **39**, 484 (1962).
[2] STRAIN, H. H., "Chloroplast Pigments and Chromatographic Analysis," (32nd Annual Priestly Lectures), Pennsylvania State University, University Park, 1958.
[3] ROUX, D. G., EVELYN, S. R., *J. Chromatog.*, **1**, 537 (1958).
[4] STRAIN, H. H., *Anal. Chem.*, **30**, 228 (1958).
[5] STRAIN, H. H., *Anal. Chem.*, **33**, 1733 (1961).

To the Editor:

It was not my intention to exclude chemical characterization as a means of identification. In the context of my article color reactions on paper were taken as a necessary condition to identification. My statement, quoted by Sherma, reads in its entirety:

> It seems reasonable to expect that some day we may have a system of organic analysis based entirely on paper chromatography. The scheme might well contain very exact relationships regarding structure and migration rate.

While I did not claim that such "relationships" are a prerequisite to identification, it does seem likely that they would prove useful in identifying the members of a homologous or other closely related series. Naturally, such an investigation would require close control of temperature, solvent composition, paper quality, etc. These requirements are within reach of today's technology.

DAVID RACUSEN

UNIVERSITY OF VERMONT
BURLINGTON

To the Editor:

In the May 1962 issue an article described the use of hypodermic syringes for an experimental verification of Boyle's law (THIS JOURNAL **39**, 252 (1962)). I should like to call attention to a similar article published by George Towe and Georgeanne R. Caughlan in the American Journal of Physics, **29**, 706 (1961).

The use of a hypodermic syringe for Boyle's law demonstration was suggested by the Physical Science Study Committee in Experiment 220 of their revision for the second portion of preliminary edition of Laboratory Guide No. 2, September 25, 1958. The Physics Laboratory at Montana State College has been using the apparatus described in the article for a number of years and it has proved to be a very satisfactory experiment.

CHARLES N. CAUGHLAN

MONTANA STATE COLLEGE
BOZEMAN, MONTANA

To the Editor:

Dr. Strong's letter (January, 1963) brings up a very important and much neglected fact about the teaching of thermodynamics. It is certainly not apparent to the student that thermodynamics is actually good for anything!

One way to increase student awareness is to have them locate and prepare a brief written report on three thermodynamic articles which have appeared in major journals within the last year. They report what was measured and how, the purpose of the research, and its importance. Typically, a class of 20 students will come up with more than 50 different articles.

JESSE H. DAY

OHIO UNIVERSITY
ATHENS, OHIO

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Chem Ed

BOOK REVIEWS

Advanced Inorganic Chemistry: A Comprehensive Text

F. Albert Cotton, Massachusetts Institute of Technology, and *G. Wilkinson*, Imperial College of Science and Technology, London. Interscience Publishers (a division of John Wiley and Sons, Inc.) New York, 1962. xv + 959 pp. Figs. and tables. $14.50.

With this latest addition to the growing literature of inorganic texts, a joint Anglo-American venture, two active contributors to the field hope to fill the need for a "comprehensive textbook . . . at an advanced level incorporating the many new chemical developments, particularly the more recent theoretical advances in the interpretation of bonding and reactivity in inorganic compounds." The authors have succeeded admirably in their goal. Particularly striking is their achievement, simultaneously, of balance, comprehensiveness, and up-to-dateness. The text is intended for students at the B.Sc. honors level in British universities or at the senior or first year graduate level in American universities and for an academic year of three 1-hour lectures per week. Its only real competitor, Durrant and Durrant's "Introduction to Advanced Inorganic Chemistry," is not as suitable for classroom use.

The book "encompasses the chemistry of all the chemical elements and their compounds, including interpretative discussion in the light of the latest advances in structural chemistry, general valence theory, and, particularly, ligand field theory." It is divided into three parts: (1) General Theory (104 pp.); (2) Chemistry of the Non-Transitional Elements (379 pp.); and (3) Chemistry of the Transition Elements (432 pp.). The last section, almost half the book, considers a class of elements which, although numerically constituting over half the periodic table, is often slighted in other texts. The coverage of theory is actually much greater than apparently indicated above, since many theoretical concepts are treated in the "descriptive" portions of the book, e.g., hydrogen bonding and acids under Hydrogen, and Fajans' rules and the diagonal relationship under The Elements of the First Short Period. In the middle section, separate chapters are devoted to the introductory elements of each group, thus effectively emphasizing their divergences from their heavier congeners. The 50-page chapter on The Theory of Metal-Ligand Bonding, with its detailed comparison of the valence bond, electrostatic crystal, ligand field, and molecular orbital theories, is easily the most unique feature of the book and is typical of the extensive treatment given to coordination compounds. The volume is replete with discussions of boranes, π-bonded compounds, organometallics, and other topics of intense current research activity. Although nomenclature, nuclear chemistry, oxidation potentials, acid-base theory, and nonaqueous solvents are usually considered in detail in more elementary texts, brief treatments of these topics would not have been out of place.

The detailed table of contents lists every section of the book, but the index seems inadequate. The book is liberally provided with equations, tables, figures, and structural diagrams; a dozen or so schematic reaction diagrams compactly summarize a great deal of diverse information. An appendix includes derivations, solutions, study problems, miscellaneous data, special references, and a supplementary reading list. The C^{12} atomic weight scale is used, and some of the references at the ends of chapters are as recent as 1962. An unusual and useful feature of this well-organized text book is the inclusion after each reference of brief evaluations and critical comments which should be helpful in orienting the student.

George B. Kauffman
Fresno State College
Fresno, California

Technik der Experimentalchemie

R. Arendt and *L. Dörmer*. 7th ed. Newly revised by *Karl-Edmund Dörmer* and *Walfried Seeger*. Quelle and Meyer, Heidelberg, 1962. 442 pp. Figs. and tables. 16.5 × 24 cm. 44 DM.

It is difficult for the American chemistry teacher, at any level of instruction, to evaluate this volume properly, since in a textual sense, there is virtually no place in our scheme of education where the material fits. Although the reviewer is calling only on limited first-hand experience, it is his impression that it is also not easy to fit the volume into a broad present-day German chemistry course. In neither the science Gymnasium nor in the Realschule (assuming a technical stress) are the students exposed to a real laboratory experience. The hundreds upon hundreds of experiments all bordering on the trivial described in "Technik der Experimentalchemie," then, are almost exclusively demonstrations to be performed by the instructional staff.

The first 70 pages of the book are devoted to general descriptions of authors' concepts of a laboratory "lay-out," apparatus for specific preparative purposes, descriptions of techniques of preparation and analysis. A section of 150 pages is devoted to non-metal chemistry. Preparation and properties of the nonmetals and their compounds are exhaustively covered. A second section covers in about 35 pages some 23 metals with both members of the representative and transition classes. The coverage given the alkali metals is typical though somewhat more extensive than that given the others. Air oxidation is demonstrated along with combustion and peroxide formation. Hydroxides are studied from the subfreshman standpoint. Carbonates are prepared by the Leblanc and Solvay process. Some quantitative experience is gained through the conversion of hydrogencarbonates to carbonates in measuring the CO_2 evolved. Little or no complex chemistry is found for the transition metals. Each section is terminated with a glimpse of classical analytical reactions. Material is documented with references only to the German literature, with one notable exception—that of THIS JOURNAL.

Following the inorganic sections there are four sections on aliphatic and aromatic organic chemistry, biological chemistry, and finally physical chemistry. This last section is little more than a survey of a few physico-chemical procedures for study-

Reviewed in this Issue

F. Albert Cotton and *G. Wilkinson*, Advanced Inorganic Chemistry: A Comprehensive Text
R. Arendt and *L. Dörmer*, Technik der Experimentalchemie
Wallace R. Brode, editor, Science in Progress, Twelfth Series
Friedrich Helfferich, Ion Exchange
Chr. Klixväll Jørgensen, Orbitals in Atoms and Molecules
Michael J. S. Dewar, Hyperconjugation
William T. Simpson, Theories of Electrons in Molecules
Paul Pascal, general editor, Nouveau Traité de Chimie Minérale. Volume 15, Part 3, Transuraniens
Paul Pascal, general editor, Nouveau Traité de Chimie Minérale. Volume 20, Alliages Métalliques. Part I
Marcel Florkin and *Howard S. Mason*, editors, Comparative Biochemistry, A Comprehensive Treatise. Volume 4, Constituents of Life, Part B, The Molecular Basis of Neoplasia
E. A. Ostroumov, translated by *D. A. Paterson*, The Application of Organic Bases in Analytical Chemistry
John J. McKetta, Jr., editor, Advances in Petroleum Chemistry and Refining. Volume 5
David M. Himmelblau, Basic Principles and Calculations in Chemical Engineering
Dudley Williams, editor, Methods of Experimental Physics. Volume 3, Molecular Physics

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ing some principles and determining some properties.

The initial material in the organic section is devoted to elementary qualitative and quantitative analysis. Preparation and properties of simlpe aliphatic and aromatic compounds are demonstrated at a level comparable to that of the inorganic demonstration. A few experiments are found for virtually all types of organic compounds—proteins, fats, carbohydrates, soaps, albumin, rubber, etc.

If the student in the age group of about 14 to 19 had, within any one of these years, the time to be exposed to this vast number of demonstrations, and if he were to have the unique co-experience of a theoretical treatment (which the reviewer is quite sure he is not), the volume would have some merit. Other books in the same language and covering this same area are available. If the authors were to spend more time in defining broad, general principles of preparative techniques, the volume would be quite unique and have considerably more merit. Fully recognizing that the German-trained chemist has few peers in preparative techniques, it would seem better for the German scientific community to devote more time to publishing material covering principles and theory, and less in the area to which this volume addresses itself.

Robert C. Brasted
University of Minnesota
Minneapolis

Science in Progress, Twelfth Series

Edited by *Wallace R. Brode.* Yale University Press, New Haven, Connecticut, 1962. xi + 331 pp. Figs. and tables. 15 × 22.5 cm. $7.50.

A quarter century ago, Yale scientist Professor George A. Baitsell initiated a series of volumes entitled "Science in Progress." Subsequently he served as editor of the first nine. This, the twelfth biennial volume in the series is based on the Sigma Xi-Resa National Lectures presented during the years 1959 and 1960 and includes a preface by the editor, Dr. Wallace R. Brode.

The well-known Sigma Xi National Lectures are intended to be of general interest to scientists and other "technically understanding" individuals rather than for the specialist. Hence, some familiarity with differential equations, thermodynamic principles, conformational analysis, nuclear phenomena and a generally solid background in the sciences are necessary for the fullest enjoyment of this volume.

Chemists and a chemical engineer have written four of the dozen lectures. However, two of these are concerned with cultural aspects of science while several others, written by authors who would ordinarily be regarded as non-chemists, present lectures in which chemistry plays a major role. As a matter of fact, one of the notable characteristics of a number of the articles is the extent to which they draw from a broad spectrum of scientific disciplines.

Chemistry Professor Cassidy discusses The Problem of the Sciences and Humanities, deplores the cultural fission developing between the scientist and the humanist, urges better communication between the two. The volume under consideration makes little if any contribution to this objective, though it should serve a useful purpose in stemming the tide of cultural fission within the sciences.

Chemist Delahay ponders some of the human factors relating to the cultivation of science—motives, methods of inquiry and evaluation of scientific achievement.

Australian Trees and Blood Pressure is the catchy title of Professor Elderfield's discussion of the methods available to the organic chemist in elucidating the structures of some of the alkaloids (potentially useful as hypotensive drugs) derived from the bark of *Alstonia.*

Chemical Engineer Dodge summarizes in a very comprehensive and scholarly fashion both the theoretical and practical problems involved in obtaining Fresh Water from Saline. The lecture is, however, a bit lengthy and the lead article of the volume by Geologist Kennedy, The Origin of Continents, Mountain Ranges and Ocean Basins maintains a better balance between scientific fact and human interest.

Botanist Dawson's Biosynthesis of the Nicotiana Alkaloids demonstrates very well the increasing importance of chemistry in the interpretations of modern biological science. This emphasis is also evident in Cell Biologist Taylor's discussion of The Problem of Chromosome Reproduction and the Problem of Coding and Transmitting the Genetic Inheritance, drawing as it does, rather freely on organic chemistry.

This volume is not written for the lay public and would hardly be recommended for the average public library. Those colleges and universities believing there is virtue in a student majoring in a science field having a feeling for the interrelationship of the sciences, might well assign a number of these lectures as required reading. The professional scientist who needs in capsule form information from the mainstreams of science outside of his field of specialization, might well consider purchasing this volume. Research scientists can perform an invaluable service to their fellow workers by writing general interest summary articles such as found in this volume.

Donald S. Allen
State University of New York
Albany

Ion Exchange

Friedrich Helfferich, University of California, Berkeley. McGraw-Hill Book Co., Inc., New York, 1962. ix + 624 pp. Figs. and tables. 16 × 23.5 cm. $16.

This is the most thorough, the most scholarly, and the best book that has appeared on this subject. It differs from "Ionenaustauscher" (1959) by the same author in being more up-to-date and in separating more sharply the qualitative explanations from the rigorous mathematical treatment. The author states in the preface, "The mathematically disinclined reader may now cheerfully skip all mathematical equations and deductions without loss of continuity. The theoretical perfectionist will, I hope, excuse the sacrifice of rigor for the sake of simplicity in qualitative explanations which were written for the benefit of his more pedestrian colleagues." Both the rigorous treatment and the qualitative explanations are done superbly well. Thus the book can serve both the casual reader who wants to obtain a broad knowledge of the properties and applications of ion exchangers and also the specialist who wants to delve exhaustively into some aspect of the general subject. If the book should fail to contain the information sought, the extensive list of references will guide the reader in further search.

The author also states in the preface, "As English is not my native tongue, I must beg the reader's forbearance regarding my style." This apology is quite unnecessary. The style and composition are better than one finds in many scientific books by American-born authors.

The titles of the chapters are: (1) Elementary Principles, (2) Structure and Properties of Ion Exchangers, (3) Preparation, (4) Capacity, (5) Equilibria, (6) Kinetics, (7) Electrochemical Properties, (8) Ion-exchanger Membranes, (9) Ion-exchange Columns, (10) Behavior in Nonaqueous and Mixed Solvents, (11) Catalysis by Ion Exchangers, (12) Electron Exchangers and Redox Ion Exchangers. The discussion covers ion-exchange minerals, synthetic inorganic exchangers, ion-exchange resins, and liquid ion exchangers. Principles rather than applications are emphasized. Each chapter includes a summary of 4 pages or less. The reviewer recommends that the reader who browses through the book start with these summaries; they will indicate to him which chapters he should study in detail.

The binding, paper, and printing are good. There are surprisingly few typographic errors.

William Rieman III
Rutgers, The State University
New Brunswick, New Jersey

Orbitals in Atoms and Molecules

Chr. Klixbüll Jørgensen, Cyanamid European Research Institute, Cologny, Geneva, Switzerland. Academic Press, Inc., London, 1962. v + 162 pp. Figs. and tables. 16 × 23.5 cm. $6.

This monograph contains a discussion of Jørgensen's ideas on chemical bonding and the "utility of electron configurations as a classification of the symmetry types and relative order of low-lying excited energy levels." All sorts of chemical compounds are discussed, with the expected bias in favor of transition metal complexes.

This book is for the "inorganic physicist," the scientist who is not only at home in the group theoretical descrip-

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tion of excited molecular energy levels but who also cares about, say, the nature of the complexes of chromium(III). It is a useful book for the mature scientist who wishes to reconsider some of his preconceptions about what electrons are doing in molecules. However, it is a difficult book to read, for Jørgensen draws from far and wide to nail down his side of each argument.

The notation is often forbidding.

Richard L. Carlin
Brown University
Providence, Rhode Island

Hyperconjugation

Michael J. S. Dewar, University of Chicago. Ronald Press Co., New York, 1962. vi + 184 pp. Figs. and tables. 14.5 × 21 cm. $6

It is an interesting, stimulating and useful exercise occasionally to re-examine various concepts extremely critically to see how well we can do without them. In this book, hyperconjugation suffers this test of fire at Professor Dewar's capable hands. The reader receives some warning that what results is not necessarily a balanced view of the problem by the author's purpose, stated in the preface, to "outline the present position in a moderately impartial manner."

Professor Dewar adopts the view that it is a purely arbitrary but nevertheless very useful description to consider valence electrons in any molecule to be localized in definite bonds and that this description should be preserved so long as it gives an accurate representation of molecular properties. Thus the delocalization of electrons of single bonds (hyperconjugation) and of *p* or *pi* electrons (conjugation) should be included as part of the electronic description only if the localized bond picture fails.

All of the main lines of evidence which have been used to support hyperconjugation are examined and alternative explanations are offered in most cases. Variations of heats of formation, bond lengths and dipole moments, which have previously been attributed to hyperconjugation, are rationalized in terms of the dependence of these bond properties on the hybridization state of carbon. Conjugation as well as hyperconjugation is judged to have an unimportant influence on these properties, "which depend on the collective behavior of valence electrons," in "classical" molecules such as 1, 3-butadiene or propene.

Although the evidence for single bond electron delocalization effects on physical properties "which depend on the behavior of individual electrons," e.g., nuclear quadrupole resonance (NQR), nuclear magnetic resonance (NMR) and electron spin resonance (ESR) spectra, is admittedly conclusive, in Professor Dewar's view "evidence of this kind has no bearing on the problem of hyperconjugation in the chemical sense."

In considering evidence from chemical reactivity the Baker-Nathan effect is dismissed as "a small second-order effect" dependent and possibly caused by several other influences such as steric inhibition of solvation; secondary isotope effect evidence is judged inconclusive since the importance of possible other factors has not been established. A detailed quantitative analysis of reactivity effects of substituents suggests that the apparent resonance effects of alkyl groups are largely inductoelectromeric in nature although hyperconjugation may be important.

Thus in the end hyperconjugation emerges stripped of much of its territory but not quite abolished. Its more powerful ally, conjugation, has incidentally sustained significant losses. One cannot help but wonder how well some of the other concepts and explanations, here admitted readily in preference to hyperconjugation, would hold up if subjected to a similarly devastating critical analysis. Of these effects perhaps inductive would survive but would inductoelectromeric?

V. J. Shiner, Jr.
Indiana University
Bloomington

Theories of Electrons in Molecules

William T. Simpson, University of Washington, Seattle. Prentice-Hall, Inc., Englewood Cliffs, New Jersey, 1962. viii + 183 pp. Figs. and tables. 16 × 23.5 cm. $6.75.

"This book is intended to fill in the gap between what is found in quantum chemistry books and what is found in the journals." Thus, this book has as a prerequisite for its readers, a rather careful perusal of some of the extensive quantum mechanics or quantum chemistry texts. This makes it a text which will be quite difficult to read for anyone but the student of quantum chemistry, and will have a relatively limited audience. For this limited audience, it is a welcome addition in its careful treatment, with great mathematical elegance, of a number of advanced problems in quantum chemistry. The author states in the preface that the aim is more in the direction of rigor than in intuitive understanding. It is surprising, however, after this statement, to find him frequently interspersing his mathematical elegance with purely intuitive statements. The bracket notation used is the most formal one known to this reviewer; it is rarely found in journal articles, but, as the author points out, is used "because it is a part of the apparatus of transformation theory."

The book is organized in four chapters; an introductory chapter on atoms, and separate chapters on the molecular orbital method, the valence bond method, and the independent systems approach. Thus, the book clearly indicates that the choice of topics treated depends not so much on their general interest, but reflects the writer's own special interests. Each chapter has its own appendix. Technically, the book has very high standards; it is well printed and well bound.

Hans H. Jaffé
University of Cincinnati
Cincinnati, Ohio

Nouveau Traité de Chimie Minérale. Volume 15, part 3, Transuraniens

Paul Pascal, general editor. Masson et Cie., Paris, 1962. 1 + 1090 pp. Figs. and tables. 17.5 × 26 cm. Broché, 180 NF. Cartonné toile, 192 NF.

Uranium and uranium compounds were described in the previous parts of this volume, and this part is concerned with the transuranium elements. It begins with an excellent introduction to the chemistry of the radioelements by Haissinsky, which includes information about the new elements and their atomic structure, radioactive transformations, nuclear reactions, physical and chemical reactions of radiations, measurements, and natural radioelements. A 25-page table of radioactive isotopes concludes the introductory material. The treatment is thorough, and the summary will be a valuable addition for reference needs.

The remainder of this part of the volume is divided into two sections: the uranides (neptunium, plutonium, and americium) and the curides (curium, fermium, mendelevium, nobelium, and the last elements of the periodic system), with additional material on lawrencium, natural atmospheric radioactivity, artificial atmospheric radioactivity, radioactive fallout, and atmospheric diffusion of fission products. Illustrations, charts, and graphs are used frequently and effectively. Literature references are numerous, and the same arrangement for these as for previous volumes has been followed by which the location of bibliography for each chapter is indicated at the bottom of each page of text.

The third part of the volume has some 1,090 pages of the more than 2,500 devoted to the entire volume. Indexing is by each individual part, and there is no cumulative index for the three. As is the case with the entire set published to this time, the indexing leaves much to be desired as to thoroughness, although it is adequate for the more general subjects. In general, few criticisms may be made, and the introductory material alone of the third part is a most valuable addition to the literature sources available to those concerned with nuclear chemistry, as well as other areas concerning radioactivity and the transuranium elements.

Roger V. Krumm
University of Florida
Gainesville

Nouveau Traité de Chimie Minérale. Volume 20, Alliages Métalliques. Part 1

Paul Pascal, general editor. Masson et Cie., Paris, 1962. 1 + 771 pp. Figs. and tables. 17.5 × 26 cm. Broché, 134 NF. Cartonné toile, 146 NF.

Volume 20 of the Pascal treatise is to be devoted to alloys, with division into three parts. The index will not appear until completion of part three, as it is intended to indicate there whether any particular alloy consists of a binary or

(Continued on page A316)

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Study Manual in Physical Chemistry

By F. E. CONDON, *The City College of New York*
April 1963, 200 pp., in preparation

This unique study manual consists of exercises based on experimental data from the original literature. It is not a book of problems in the usual sense. Rather, the student is given a set of data and guided in its application to the solution of specific problems or the determination of constants. This new approach to teaching exposes the student to results actually obtained in the laboratory and provides him with practice in the application of principles presented in the classroom to these results.

Examination copies for classroom adoption are available upon request.

Physical Methods in Heterocyclic Chemistry

Edited by A. R. KATRITZKY, *Cambridge, England*

Volume 1—NONSPECTROSCOPIC METHODS
January 1963, 346 pp., $12.00
Volume 2—SPECTROSCOPIC METHODS
Spring 1963, 398 pp., $14.00

Physical Methods in Heterocyclic Chemistry concentrates in one convenient work reliable guides to the physical methods useful in heterocyclic chemistry. The coverage is extensive and the treatment detailed—numerous tables and references are included.

This treatise is directed to the organic chemist, enabling him to make advantageous use of the new techniques available. In this respect the volumes will be invaluable for their concentration of information heretofore scattered in many different publications.

A Statistical Manual for Chemists

By EDWARD L. BAUER, *Withrop Laboratories, Rensselaer, New York*
1960, 156 pp., $4.75

Review:

"The author in his preface describes this book as 'a manual for the working chemist' and no more exact definition of this excellent little handbook could possibly be given. Shorn of all complicated mathematical functions and lucid in its approach, this volume supplies the chemist with typical examples taken from ordinary laboratory data, and indicates those benefits relating to economy, accuracy and interpretation which can accrue from applications of the statistical method. This book should prove a most useful elementary introduction to the amateur statistician, particularly in the chemical field."

—*Nature*

Energy

By BRUCE CHALMERS, *Division of Engineering and Applied Physics, Harvard University*
April 1963, 289 pp.

This book is the first to treat the subject of energy in all of its aspects. It describes and explains the many forms in which energy can exist; how it is stored, transmitted, and exploited; how it can be converted from one form into another; and the part it plays in this technological world. The treatment, although quantitative, involves a minimum of mathematics. The possibilities and limitations inherent in future developments are discussed. Energy resources of the world and the problem of their adequacy in the future are also considered. The inclusion of problems of various levels of difficulty is a helpful feature for teachers and students as well as for the general reader.

Although designed primarily as an undergraduate text for courses serving as an introduction to the physical sciences, this volume will provide useful background material for many other courses in related areas.

Mass Spectrometry of Organic Ions

Edited by F. W. MCLAFFERTY, *The Dow Chemical Company, Framingham, Massachusetts*
March 1963, 730 pp., $24.00

This volume is concerned with the chemistry and physics of organic ions—a challenging new field made possible largely by the development of mass spectrometry. It treats both the basic theories and the significant applications of this unique method in organic systems. Up-to-date, authoritative information is given on the formation, decomposition, reactions, and properties of positive and negative organic ions. The book also includes the applications of the underlying principles to major problems in such fields as radiation chemistry, high energy reactions, kinetics, thermodynamics, free radicals, and molecular structure.

The Chemistry of Heterocyclic Compounds

By G. M. BADGER, *University of Adelaide, Adelaide, South Australia*
Volume 5 of ORGANIC AND BIOLOGICAL CHEMISTRY: A Series of Monographs
Edited by LOUIS F. FIESER and MARY FIESER
Harvard University
1961, 498 pp., $12.00

Review:

". . . this is a splendid book containing copious references and much useful material. It is one which can certainly be recommended both to undergraduate and graduate students."

—*The Industrial Chemist*

ACADEMIC PAPERBACKS

DIVISION OF LABOR IN CELLS
G. H. BOURNE
1962, 248 pp., $2.95

TIME, CELLS, and AGING
B. L. STREHLER
1962, 270 pp., $2.95 (Clothbound $5.00)

DESIGN AND FUNCTION AT THE THRESHOLD OF LIFE: THE VIRUSES
H. FRAENKEL-CONRAT
1962, 144 pp., $1.95

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LONDON Berkeley Square House, London, W.1

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A PROGRAMMED TEXT IN NUMBERS AND UNITS FOR SCIENCE

By Frank E. Harris, *Stanford University*

This program deals with:

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more complex combination. This part of the volume describes the crystallography of alloys in general and then presents data on the alkali metals, alkaline earths, transition metal alloys, and some alloys of magnesium, as well as aluminum.

Over 5000 literature references are cited, and in many cases the gap from the date of the final search to the date of publication is not large, although in others several years have passed. The diagrams and figures number some 350, and they are particularly abundant and excellent in the section on crystallography. Phase diagrams are also stressed. The arrangement of chapters has been made to group metals, or families of metals, with common characteristics. The alloys of metals with metalloids are taken up in some detail in the sections on alkali metals and alkaline earths.

For the material covered up to this point, the volume would seem to be thorough in coverage, well illustrated, and excellent in many respects, but an evaluation of the volume as a whole cannot be made until the entire work can be examined. The material presented appears to be up to date, and the high standards of the entire treatise previously published have been maintained.

ROGER V. KRUMM
University of Florida
Gainesville, Florida

Comparative Biochemistry, A Comprehensive Treatise. Volume 4, Constituents of Life, Part B

Edited by *Marcel Florkin*, University of Liège, Belgium, and *Howard S. Mason*, University of Oregon Medical School, Portland. Academic Press, Inc., New York, 1962. xxiii + 841 pp. Figs. and tables. 16.5 × 23.5 cm. $26.

Volumes 3, 4, and 5 of "Comparative Biochemistry" are concerned with the principal classes of constituents of organisms and their biological transformations. In keeping with this theme, Volume 4, like Volume 3, continues a treatment of metabolic components which are ubiquitous and which emphasize the essential biochemical unity of life. Thus, there are several chapters which illustrate this unity, including discussions devoted to cellulose, starch and glycogen, lignin, the nucleic acids, aromatic amino acids, the porphyrins, pteridines, and carotenoids. At the same time, however, the current volume also begins to treat those metabolic constituents which occur only in portions of the phylogenetic scale and which remind us that there is also a biochemical diversity in life. It might be helpful to the reader to underscore a few of the chapter topics which fall into the latter category.

Volume 4 begins with a delightful review of optical asymmetry and its relevance to the origin and evolution of living things. One of the best written chapters in the current volume is that

(Continued on page A318)

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New and Forthcoming BOOKS from McGraw-Hill

☐ **ION EXCHANGE**

By FRIEDRICH G. HELIFFERICH, Shell Development Company. McGraw-Hill Series in Advanced Chemistry. 624 pages, $16.00.

A revised translation of the author's German text, this book provides the first comprehensive unified treatment of ion exchange, covering the fundamental principles, structure, preparation and theory. It conveys a thorough understanding of the phenomena and their physical causes, a feeling for the behavior of ion exchangers, and the physico-chemical tools which are helpful in applying ion exchangers in practice. The theoretical treatment proceeds along two parallel lines of approach: qualitative reasoning and quantitative mathematical treatment.

☐ **INTRODUCTION TO CHEMICAL INSTRUMENTATION**

By EDWARD J. BAIR, Indiana University. McGraw-Hill Series in Advanced Chemistry. 349 pages, $10.75.

An introduction for the experimental chemist to a detailed understanding of the design and operation of chemical instruments. Emphasis is on the flow of signals and the information they represent. Designed for graduate students and research workers, the book covers a representative collection of topics which should give the student an insight into new advances in instrumentation as they appear in chemical literature, and an insight into the art of designing instruments for new applications.

☐ **PHYSICAL ORGANIC CHEMISTRY, Second Edition**

By JACK HINE, Georgia Institute of Technology. McGraw-Hill Series in Advanced Chemistry. 576 pages, $11.50.

As before, this widely known textbook is designed for graduate students who have completed elementary organic and physical chemistry. It discusses mechanisms of organic reactions and the effect of changing reaction variables, especially reactant structures, on reactivity in these structures. All material has been thoroughly updated. Changes include: expanded treatment of kinetics and its relation to reaction mechanisms; increased material on quantitative correlations of reaction rates and equilibria, and more information on methylenes.

☐ **EXPERIMENTS IN PHYSICAL CHEMISTRY**

By DAVID SHOEMAKER and CARL W. GARLAND, both of Massachusetts Institute of Technology. 480 pages, $8.95.

Suitable as a text for advanced physical chemistry laboratory courses. Each of the 44 class-tested experiments is accompanied by theoretical development, providing a lucid understanding of the method, the calculations, and the significance of final results. Both traditional and modern experiments are included. The book also contains supplementary material concerned with modern apparatus and techniques in physical chemistry.

☐ **INORGANIC SYNTHESES, Volume VII**

By JACOB KLEINBERG, University of Kansas. 352 pages, $8.95.

Contains sixty-five contributions covering a wide range of compounds and emanating from a large number of laboratories both in this country and abroad. As in other volumes of the series, each synthesis has been carefully checked in a laboratory other than that from which it was submitted. Also in accordance with established practice, the syntheses in Volume VII are arranged on the basis of the Mendeleeff periodic classification, with subdivision into A and B groups. The subject and formula indexes in this volume are cumulative for all seven volumes. The book describes tested methods for the preparation in high purity of inorganic compounds of potential value to the research chemist. Moreover, it will be valuable as a source of compounds and techniques for courses on an advanced level in inorganic preparations.

☐ **INTRODUCTION TO WAVE MECHANICS**

By LOUIS HARRIS and ARTHUR I. LOEB, both of Massachusetts Institute of Technology. Available in May, 1963.

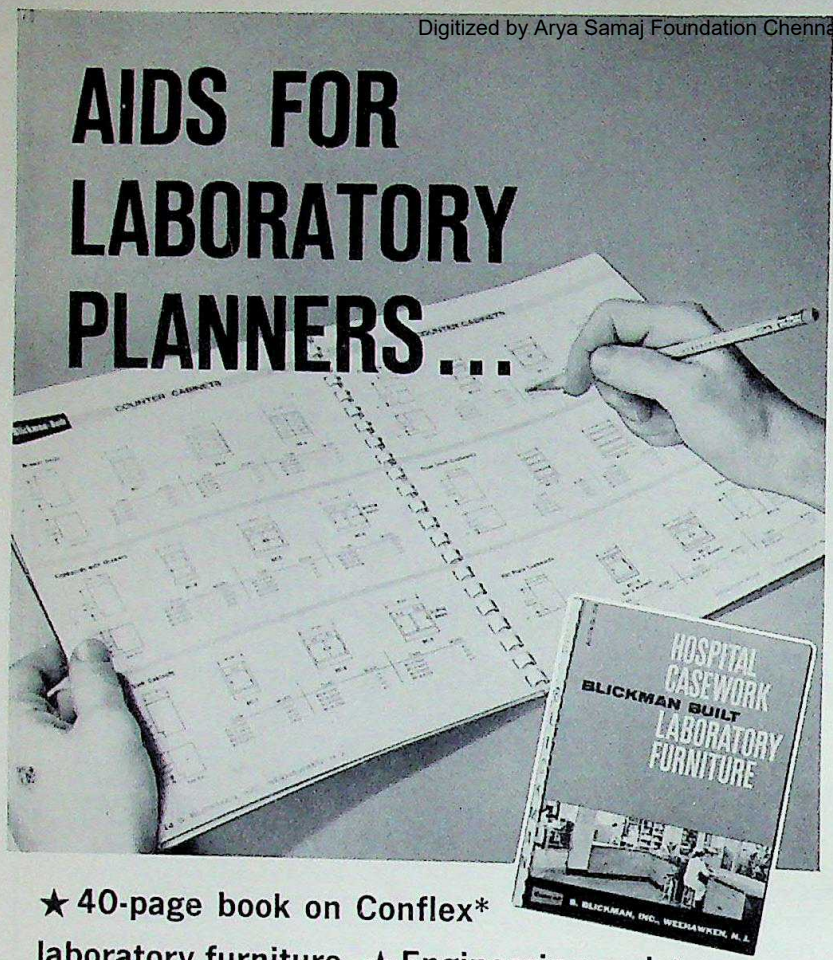
A self-contained textbook for a one-semester course, presenting most of the principles of non-relativistic wave mechanics, with examples illustrating applications of these principles. It is intended for students having a background of about two years of college mathematics and physics, including atomic physics. The authors have aimed at a logical sequence of topics, and a detailed discussion of each. Important principles are first illustrated by examples, and then again by problems interspersed throughout the text. Emphasis is more on depth in detail than on a broad coverage of topics.

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entitled Protein Molecules: Intraspecific and Interspecific Variations, including a consideration of both homologous and heterologous proteins. Other chapters devoted to more specialized forms of proteins include those on keratin, sclerotization, and blood coagulation. This group of chapters on special forms of adaption of protein structure is rounded out by an excellent critique of problems of metamorphosis and biochemical adaptations in amphibia. The present volume closes with a review of the comparative biochemistry of the alkali metals and a discussion of the evolution of ion balance in intra- and extracellular fluids.

The continued high quality of scholarship evident in Volume 4 of "Comparative Biochemistry" gives the subscriber to all seven volumes an exciting anticipation of soon having in his library the most comprehensive and critical treatise to be written in this area during the past two decades.

W. R. Frisell
University of Colorado
School of Medicine
Denver

The Application of Organic Bases in Analytical Chemistry

E. A. Ostroumov. Translated by *D. A. Paterson.* Pergamon Press Ltd., London, 1962. xxv + 159 pp. Tables. 14.5 × 22 cm. $8.50.

This monograph is a detailed, retrospective, somewhat personalized presentation of certain systematic studies pursued by E. A. Ostroumov since about 1933. These studies were directed toward the use of weak organic bases for *p*H control and adjustment and as weak complexing agents in the hydroxide and sulfide precipitations of metals. In brief, methods are presented for the somewhat selective separation of certain metals based on the use of pyridine or 2-picoline in hydroxide precipitations and of pyridine or hexamethylenetetramine in hydrogen sulfide precipitations. Some of the findings are of lessened contemporary importance with the evolution of such techniques as precipitation from homogeneous solution ion exchange, and solvent extraction.

Because of the limited audience to which this monograph should be of primary interest, the translator and his publisher are to be especially commended for this undertaking. The translation into Western European languages of Russian monographs for the specialist often aids far more in surmounting communication barriers than the translation of many works of broad readership.

Brief, page-to-page comparison of the original Russian work, published in 1959, and the English text indicates that the translation is complete and felicitous.

A. J. Barnard, Jr.
J. T. Baker Chemical Co.
Phillipsburg, New Jersey

(*Continued on page A220*)

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What should a non-science major know about nucleoproteins . . . DNA . . . glycogenesis?

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Instead of the conventional study of inorganic chemistry usually offered to freshmen students, Dr. Routh places emphasis on all three fields—*inorganic, organic, and biological chemistry.* So skillfully has the subject been covered that the presentation is thoroughly understandable and inviting even for students new to science.

In addition to thoroughly revising every section of the book, the author has added two new chapters on Nucleic Acids and Enzymes. Almost all of the illustrations are new for this edition; the format has been enlarged and improved.

By JOSEPH I. ROUTH, Ph.D., Professor of Biochemistry, State University of Iowa, Iowa City, Iowa. About 480 pages, 6⅝" × 9¼", with about 277 illustrations. About $8.50.

New (3rd) Edition—Ready April, 1963!

Noller's STRUCTURE AND PROPERTIES OF ORGANIC COMPOUNDS

Here is a brief new survey text ideally suited to a one-semester course in organic chemistry. It provides solid information on material carefully selected for non-chemistry majors. Only those syntheses used in the production of common chemical compounds are described. The emphasis in the text has been placed on bonding and structure, and on those physical and chemical properties of materials that the student is most apt to encounter in his daily experiences.

The author emphasizes bonding and structure and answers such questions as: What is the constitution of a substance? What is its source? What are the substance's chemical and physical properties in terms of the ordinary contacts the students will have with it? Discussion of aliphatic, aromatic, alicyclic and hetercyclic compounds are skillfully integrated into the text.

By CARL R. NOLLER, Ph.D., Professor of Chemistry, Stanford University. 255 pages, 6⅞" × 9¼", illustrated. $6.00.

Published February, 1962.

How much math do chemistry majors need to know?

Hutchinson's PHYSICAL CHEMISTRY

Dr. Hutchinson believes that students should have a firm grasp of differential and integral calculus and partial differentials to major in chemistry and particularly before taking a course in physical chemistry.

In his text, the author shows how this knowledge enables the student to treat many subjects (e.g., the derivation of many results in thermodynamics and the treatment of X-ray diffraction) with much greater clarity and rigor than is otherwise possible.

Unified thermodynamics forms the basis for this rigorous physical chemistry text. The author does not fill his book with endless recitations of chemical reactions and phenomena. He opens with a discussion of macroscopic systems in which reactions are occurring. There is specific information on simple- and complex-order gas reactions, straight chain and branched chain reactions, reactions in solutions, the collision theory and activated state theories of reactions. The author then covers those systems which are intermediate between the macroscopic and the molecular.

The remainder of the book sets forth the details of atomic and molecular processes, atomic and molecular spectra, wave mechanics and chemical bonding.

By ERIC HUTCHINSON, Ph.D., Professor of Chemistry, Stanford University. 647 pages, 6⅝" × 9¼", 238 illustrations. $10.00.

Published May, 1962.

Gladly sent to college teachers on approval!

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The Molecular Basis of Neoplasia

Published for The University of Texas M. D. Anderson Hospital and Tumor Institute. University of Texas Press, Austin, 1962. 614 pp. Figs. and tables. 15.5 × 23.5 cm. $10.50.

This fascinating book, a publication of the papers presented at the Fifteenth Annual Symposium on Fundamental Cancer Research (1961), consists of half a dozen articles on each of the following topics: Nucleic Acids, Nucleic Acids and Proteins, Protein Conformation and Sequence, Controlling Mechanism and Enzyme Synthesis, Controlling Mechanisms and Biochemical Alterations Induced by Viral Nucleic Acids, and Ribosomes and Protein Synthesis, as well as the Bertner Foundation Lecture, on the Enzyme Deletion Hypothesis of Carcinogenesis, by Van Potter.

Although the book is entitled "The Molecular Basis of Neoplasia," much of the work is so fundamental that neoplasia is not even mentioned in many of the papers. No matter; each paper consists of a nice balance of experimental detail and theoretical reflections, and almost every paper is so well done that it is impossible to single out any as the most interesting or most important.

The proper appreciation of much of the work requires a background in bacterial genetics, nucleic acid structure, protein synthesis, or physical chemistry, but almost everyone with even a slight knowledge of some of these subjects will get much from the book. Numerous references enhance the value of the papers.

The paper and printing are excellent indeed, and typographical errors are almost absent.

PETER OESPER,
Hahnemann Medical College
Philadephia, Pa.

Advances in Petroleum Chemistry and Refining. Volume 5

Founded by *Kenneth A. Kobe* and *John J. McKetta, Jr.* Edited by *John J. McKetta, Jr.*, University of Texas, Austin. Interscience Publishers (a division of John Wiley) New York, 1962. xiv + 545 pp. Figs. and tables. 16 × 23.5 cm. $20.

Like other "Advances" books, this volume consists of a variety of loosely related articles that are either general surveys or reviews of the recent literature.

The first chapter presents the history of synthetic fuels (fuels produced from nonpetroleum sources), points out the major developments in the field, and summarizes the current status. It constitutes a good initial reference for anyone who is about to work in the field of synthetic fuels or in related fields.

The second and third chapters are survey articles on the uses of computers in process design and in petroleum refining. They describe how computers work and how they are applied in these two fields. Both chapters could be used as computer-application references for survey courses.

Chapter four is a well-written discussion of atomization. It should be an excellent reference for anyone undertaking work in this field.

The fifth chapter is a qualitative discussion of the mechanism of catalytic cracking, with emphasis on secondary reactions. It should be a useful reference for new workers in the field.

Chapter six is a survey of the chemistry, refining, and uses of petroleum asphalt.

Chapter seven presents a review of recent literature on the reactions of olefins, with emphasis on those of commercial significance. It should be useful to anyone working in the field.

The eighth chapter is a comprehensive discussion of the applications of shock tubes, plasma jets, and ballistic pistons to light hydrocarbons. In addition to describing these devices and how they are used, the article summarizes the data reported for their use on light hydrocarbons.

The ninth chapter is a qualitative discussion of recent developments in the manufacture of nitrogen fertilizers from petroleum raw materials, with references to articles where specific information can be found.

The final chapter describes the development of small gas turbines. Sufficient details are given to give the uninitiate a general picture of how small gas turbines developed, the problems of such turbines, and what future developments might be.

(*Continued on page A322*)

Teachers of College Inorganic Chemistry

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by R. B. HESLOP and P. L. ROBINSON

Here, in one volume, is an outline of inorganic chemistry which treats the subject fully for advanced students and also assists teachers planning instruction on several levels. The authors have taken full account of the necessity for describing chemical phenomena in terms of atomic physics, quantum mechanics, and theoretical and physical chemistry. The book furnishes a brief account of every element, readily assimilated information about selected groups of elements, and a number of topics chosen to bring related material together. Valency and structure are illustrated liberally by specially drawn diagrams, and there are many tables, all presented concisely. Major additions to this edition which will be published on Aug. 1, 1963 are a description of phosphonitrilic compounds, a section on complexes in aqueous solution, and a chapter on inorganic polymers. It has been adopted in more than 100 classrooms throughout the world.

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NEW CHEMISTRY BOOKS FROM PRENTICE-HALL

CHEMISTRY for the APPLIED SCIENCES *by Katherine B. Hoffman, Florida State University*

This new text probes the composition, structure and properties of matter—relating them to the behavior of living cells. *Outstanding features:* employs the language of modern chemistry / teaches types of bonding and their influence on chemical and physical properties / uses an orbital approach to atomic structure / includes a chapter on drugs / discusses coordination complexes, oxidation-reduction, energy changes, nuclear chemistry, and radiation effects / is organized into inorganic, organic, and biochemistry sections, unified by a chapter on the composition and structure of the cell. *January 1963, 448 pp., Text Price: $7.95*

HOW to SOLVE GENERAL CHEMISTRY PROBLEMS, 3rd Ed.

by C. Harvey Sorum, University of Wisconsin

Emphasizing the mole approach to the solution of all problems, this self-teaching text gives detailed explanations of how to go about solving the various types of problems in general chemistry—ranging from the elementary to the more rigorous problems in honor courses. *January 1963, 272 pp., Paperbound, Text Price: $2.95*

ELEMENTARY CHEMISTRY

by Marcel W. Nathans, Lawrence Radiation Laboratories

"The treatment avoids extensive use of deductions from atomic structure theory because of the difficulty of many of the theoretical ideas, particularly for beginning students. Complicated organic formulas have been held to a minimum, and the emphasis placed on the concept of functional groups. *February 1963, 407 pp, Text Price: $7.25*

CHEMISTRY, 2nd Ed.

by James V. Quagliano, Florida State University

The new edition of this widely-adopted text presents unusually clear discussions of descriptive chemistry and introduces at an elementary level three particularly important features: the concept of Equilibrium, Oxidation Potentials, and the Shapes of Molecules and Ions. Ionization and Electrolysis, and Oxidation-Reduction Half Cells are carefully interwoven, thoroughly explained. A new chapter dealing with additional metal and nonmetals and their compounds has been added.

AMONG THE FEATURES

- The nonmenclature of oxyacids and a brief introduction to the periodic table are covered in the early chapters.
- Exercises and problems at the end of each chapter are now separated into two groups for convenience.
- Dimensional drawings added and many other illustrations revised for clarity.
- Chapter on Electrolysis and Half Cells improved with additional equations.

March 1963, 912 pp., Text Price: $7.95

CHEMICAL CONCEPTS and SELECTED PRINCIPLES of CHEMISTRY

both By Jay A. Young, Kings College

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The student is provided with a totally different approach, since these are among the first books of programmed instruction in chemistry.

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Wherever possible, reference is made to the laboratory, either directly or indirectly, since the laboratory is the final arbiter in any discourse about chemistry.

The work relies heavily up the principle that theories depend up facts, not the converse.

These books are intended for use as adjuncts to any standard introductory chemistry textbook.

May 1963, approx. 128 pp., Paperbound, Spiral Binding, Text Price: $2.95 each.

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Prognostications concerning the potential of gas turbines in automobiles are, however, conspicuously absent.

For university libraries, no general recommendation can be made concerning this volume. Whether or not it would be useful depends upon the particular curricula and upon the availability of other sources of the information presented in this volume. For those libraries that include earlier volumes of this series, this reviewer recommends that the frequency of their use be ascertained before a decision is made concerning this volume.

R. J. Hengstebeck
American Oil Company
Whiting, Indiana

Basic Principles and Calculations in Chemical Engineering

David M. Himmelblau, University of Texas, Austin. Prentice-Hall, Inc., Englewood Cliffs, New Jersey, 1962. viii + 459 pp. Figs. and tables. 15.5 × 23.5 cm. $9.75.

It requires courage and conviction to prepare a manuscript in a field already as well covered by texts as is the first chemical engineering mathematics course. It is, therefore, a mark of outstanding ability to be able to write a text which will not only successfully enter the field but will unquestionably challenge the leadership of the older texts in this area. Dr. Himmelblau has demonstrated this ability in the preparation of this text.

Actually, there is not much to be added to the subject of beginning calculations. The general principles, and even the problems, are of such a standard character that there can be little of the new or the novelty in the subject material itself. Hence, emphasis must be placed on the method of presentation. In this Dr. Himmelblau has excelled. A free and rather informal discourse leads to the logical development of illustrative problems, there being at least one problem to demonstrate the application of each of the principles introduced. The solution of each illustrative problem is so clearly and adequately presented that the average student should be able to solve the practice problems with a minimum of supplemental instruction.

The text consists of six chapters and a well selected group of tables of data as a supplement. The subject matter coverage of the first five chapters is approximately normal for the course for which the text is obviously written and is closely comparable to that of other texts in this field. The subjects of introductory calculations, material balances, the phenomena related to gas laws, vapor pressure and phase phenomena, energy balances, and combinations of the material and energy balances are certainly standard for a chemical engineering course at the beginning level. Each subject is covered in adequate depth and the work is arranged in such a manner that the individual instructor can readily tailor a course to fit the time allocated in his particular curriculum to introductory chemical engineering calculations. Dr. Himmelblau's sixth chapter is one dealing with the unsteady state material and energy balances. This is something of an innovation, although a welcome one, for the work in stoichiometry. It will be very useful providing the student using the text has had an appropriate background in mathematics.

A short section near the end of each chapter, in which there is summarized the principles the student should have learned in that chapter, is an interesting addition to the text. The compilations should be thought provoking to the student.

Each chapter has a list of supplementary references. Since these references are mostly other texts, the list is repeated, without much difference, at the end of each of several chapters. These references could be improved, if they are to be added in this fashion, by citation of page or chapter.

The practice problems at the end of each chapter, a total of over four hundred, are certainly adequate in number. They are clearly and concisely presented, and they appear to be graded carefully in complexity.

In the way of recapitulation, the straightforward presentation combined with a writing style of such a nature as to promote easy reading, the well-organized

(*Continued on page A324*)

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1963 Approx. 630 pages. Prob. $7.95

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arrangement of text and problems, and the unusually good explanation of the illustrative problems make this an excellent text. Fine printing of an easily readable type on high quality paper has produced a book which is a compliment to the printer's skill.

This is a text which should find immediate adoption by many chemical engineering departments. It has been written essentially for students. To his credit the author has not attempted to make it anything else.

B. E. Lauer
University of Colorado
Boulder

Methods of Experimental Physics. Volume 3, Molecular Physics

Edited by *Dudley Williams*, Ohio State University, Columbus. Academic Press, Inc., New York, 1962. xiv + 760 pp. Figs. and tables. 16 × 23.5 cm. $19.

This is one volume of a six-volume series covering the various areas of experimental physics. Of the six this is probably the one of greatest interest to chemists. The major areas covered in this volume are: Molecular spectroscopy (microwave, I. R., Raman, electronic), Resonance studies (NMR, electron spin resonance, quadrupole resonance), Mass spectrometry, Molecular beams, Electric properties, and Ultrasonic studies.

The material included is quite up-to-date, including such recent innovations as the use of optical masers as Raman light sources. Also, since each chapter is written by someone in the field involved, fairly complete coverage of each area is insured. The general approach in each chapter is to give a fairly thorough theoretical description of the particular phenomenon followed by a discussion of the various experimental techniques used with references to the original work of many of the investigators in the field.

The book is obviously written for physicists and is concerned primarily with the various physical phenomena and spends little time dealing with the applications of the techniques. It is for just this reason, however, that it can be of value to the chemist. All too often the powerful tools of modern structure determination are used by people who do not thoroughly understand the underlying principles and methods involved in the technique that they are using. The result is often incorrect interpretation of the data and the subsequent inclusion in the literature of information which must later be corrected.

This volume treats the subject at a fairly high level but the treatment is generally quite clear so that one need not be a mathematical physicist to understand it. It should be of particular value to chemists interested in the area of structure determination as a convenient reference to all of the modern techniques and the manner in which they relate to the underlying theory.

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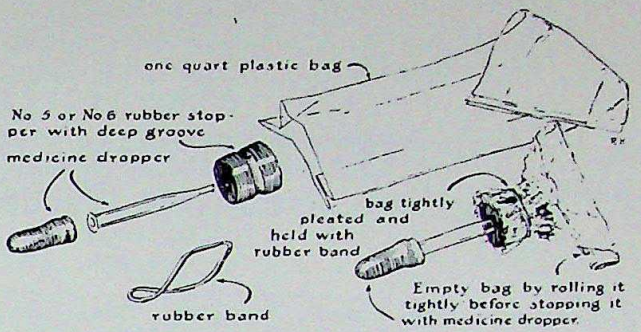
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Paperback Books in Chemistry and Related Sciences

THE paperback revolution which so drastically has changed the conduct of courses in the humanities is now beginning to affect the sciences. (See THIS JOURNAL, **37**, 327 (1960)).

For many years the science offerings on the paperback shelves have been strictly collateral reading for most courses (philosophy or history of science). Then a few years ago reprints of former chemical "classics" began to appear. Also numerous excellent treatments of chemical subjects written for the layman are so well done that chemists in other specialties find them rewarding. Most recently books which have been written as textbooks or text supplements are beginning to appear.

The accompanying list has been prepared in cooperation with publishers in the hope that readers will find it useful in planning present and future courses. We earnestly solicit comments from readers. If the response so indicates, it can become a valuable annual feature.

We repeat with emphasis the view expressed in "Editorially Speaking" THIS JOURNAL, **39**, 545 (1962):

> "Imaginative and well planned innovations require conviction and courage. When publishers team with classroom chemists to give such solid evidence of these qualities, it earns the applause of all. The applause that really counts will be the support of those equally imaginative enough to take advantage of these new tools for better chemistry instruction."

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Harrison, K. *A Guidebook to Biochemistry.* 1959 150 pp $1.95 Cambridge University Press.

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Anderson, H. V. *Chemical Calculations.* 1962 305 pp $2.75 McGraw-Hill Book Co., Inc.

Barrow, G. M. *Structures of Molecules.* 1963 144 pp $1.95 W. A. Benjamin, Inc.

Belcher, J. E., Colbert, J. C. and **Rowley, H. H.** *Experiments and Problems for College Chemistry.* 6th Edition 1961 264 pp $3.75 Appleton-Century-Crofts.

Belcher, J. E., Colbert, J. C. and **Rowley, H. H.** *Properties and Numerical Relationships of the Common Elements and Compounds.* 6th Edition 1961 384 pp $4.25 Appleton-Century-Crofts.

Boys, C. V. *Soap Bubbles and the Forces Which Mould Them.* 1959 $.95 Science Study Series. Doubleday & Co., Inc.

Brumblay, Ray U. *Quantitative Analysis.* 1960 235 pp $1.50 Barnes & Noble, Inc.

Bush, George L. and **Silvidi, Anthony A.** *The Atom: A Simplified Description.* 1961 147 pp $1.25 Barnes & Noble, Inc.

Curie, Marie. *Radioactive Substances.* 1961 96 pp $.95 Philosophical Library.

Davis, Kenneth S. and **Day, John Arthur.** *Water: The Mirror of Science.* 1961 $.95 Science Study Series. Doubleday & Co., Inc.

Davis, W. Merrill and **Smith, Herbert R.** *Chemistry in Review.* 1962 416 pp $1.40 Lyons & Carnahan.

Faraday, Michael. *The Chemical History of a Candle.* Explorer Edition 1960 128 pp $.85 The Viking Press, Inc.

Feifer, Nathan. *Let's Explore Chemistry.* 1959 128 pp $1.00 Sentinel Books, Inc.

Findlay, A. *Chemistry in the Service of Man.* $1.75 Harper Torchbook.

Fitzgerel, Robert K., Compiler and **Kieffer William F.,** Editor. *Supplementary Readings for Chemical Bond Approach.* 206 pp Single copies, $3.00 each; 10–19 copies, $2.65 each; 20 or more copies $2.25 each. Chemical Education Publishing Co.

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Hill, R. D. *Tracking Down Particles.* 1963 208 pp $2.95 W. A. Benjamin, Inc.

Holden, Alan and **Singer, Phylis.** *Crystals and Crystal Growing.* 1960 $1.45 Science Study Series. Doubleday & Co., Inc.

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Jaffe, Bernard. *Crucibles, The Story of Chemistry.* 1962 240 pp $.50 Premier Books, Fawcett Publications, Inc.

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King, E. L. *How Chemical Reactions Occur.* 1963 144 pp $1.95 W. A. Benjamin, Inc.

Lessing, Lawrence P. *Understanding Chemistry.* 1959 192 pp $.60 Signet Science Library Book The New American Library of World Literature, Inc.

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Ryschkewitsch, G. E. *Chemical Bonding and the Geometry of Molecules.* 1963 128 pp $1.95 Reinhold.

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Katz, J. and **Rabinowitch, E.** *The Chemistry of Uranium.* 1961 609 pp $2.95 Dover.

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Asimov, Isaac. *Marvels of Science.* $.95 The Crowell-Collier Publishing Co.

Garatt, Arthur, Editor. *Penguin Science Survey.* 1961 Volume I 238 pp $1.45 Houghton Mifflin Co.

Gensler, W. J. and **Gensler, K. D.** *Writing Guide for Chemistry.* 1962 159 pp $2.95 McGraw-Hill Book Co., Inc.

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Uvarov, E. B. *A Dictionary of Science.* 240 pp $.95 Houghton Mifflin Co.

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Asimov, Isaac. *The World of Carbon.* 1962 Revised Edition $.95 The Crowell-Collier Publishing Co.

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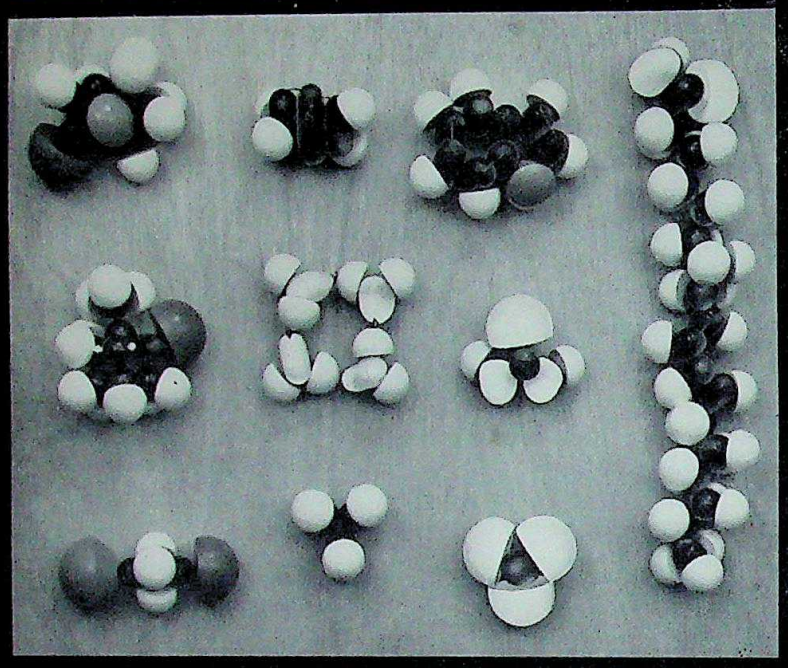
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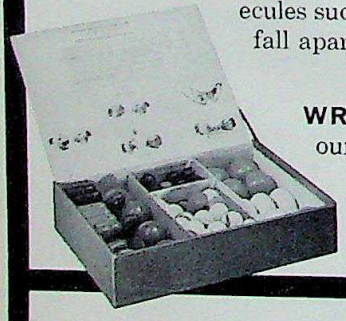
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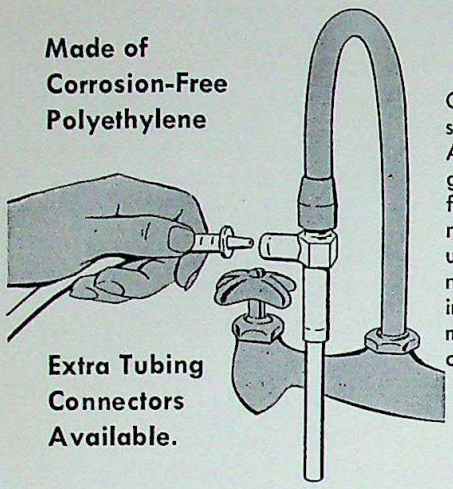
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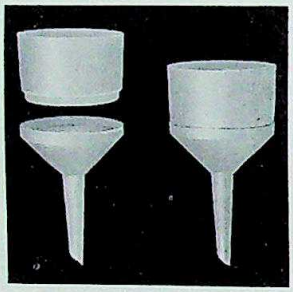
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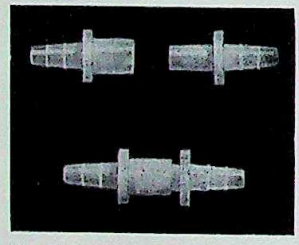
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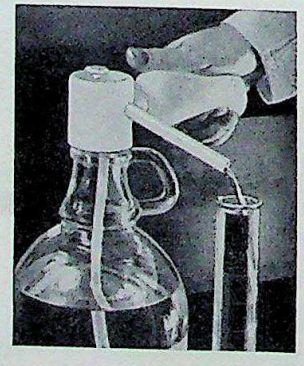
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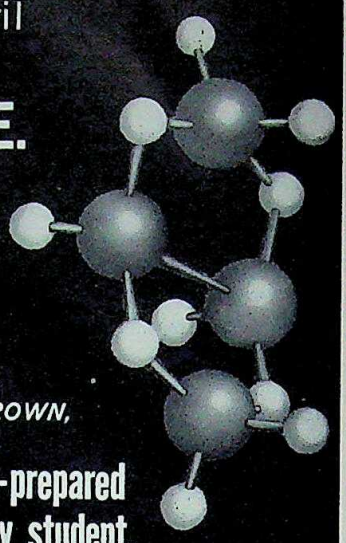
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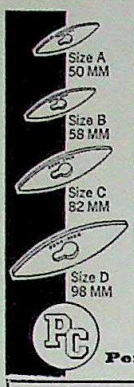
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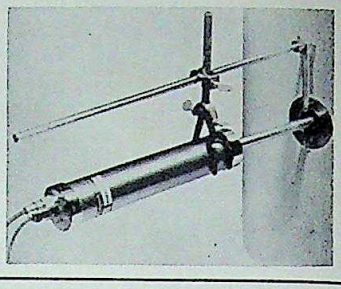
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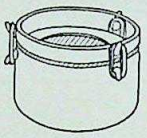
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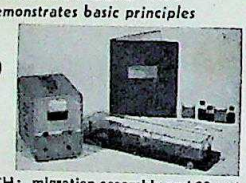
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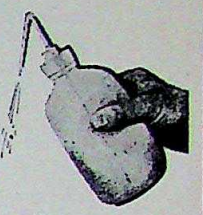
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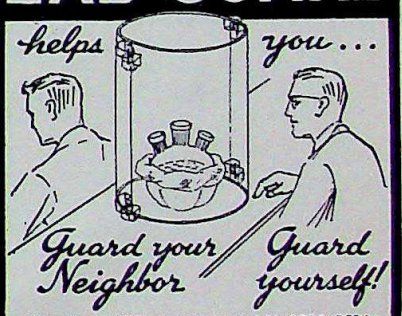
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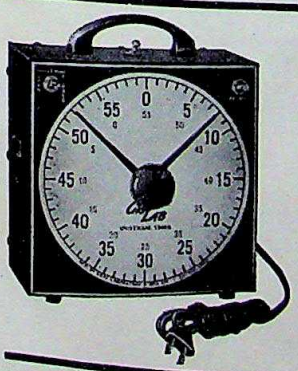
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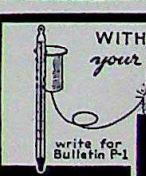
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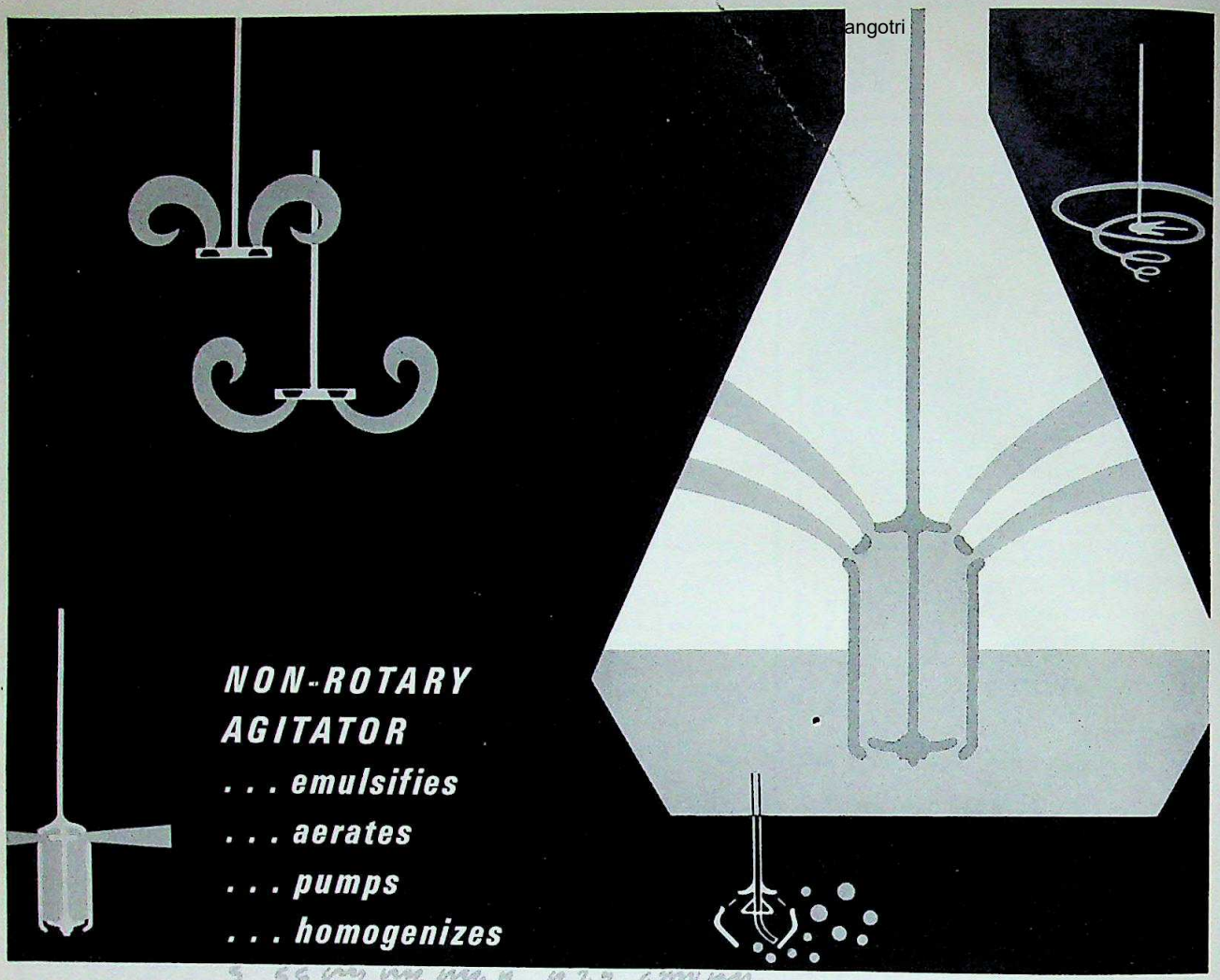


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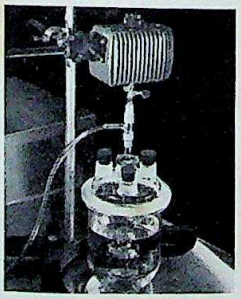


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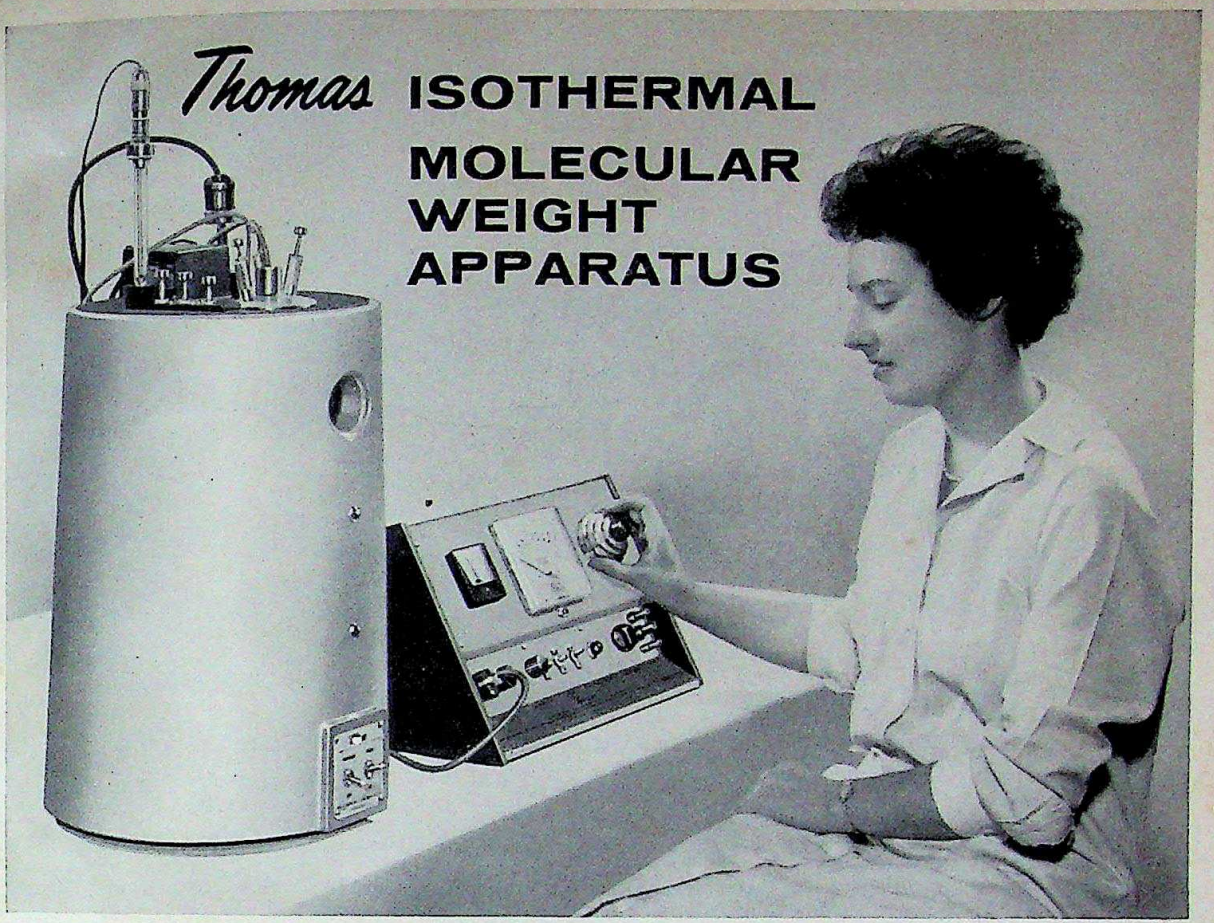
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Technique. Two thermistors are used to measure temperature difference between solvent and solution in a solvent vapor chamber thermostatically controlled within ±0.003°C. Samples are applied to thermistor tips by means of micrometer syringe pipets. Provision is made for delivery of solvent to both thermistors, and for subsequent delivery of solution to the measuring thermistor. Readings made with only two dilutions of a known sample suffice to establish the molar constant for a given solvent. Change in measuring thermistor resistance is made by means of a high-sensitivity d.c. resistance bridge. Molecular weight can be calculated directly using the resistance value obtained. *Conversion to temperature units is not required.*

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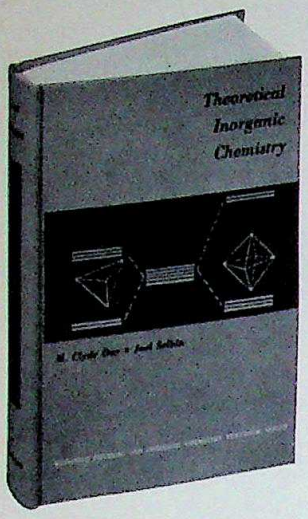
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Edited by S. Z. LEWIN, New York University, New York 3, N. Y.

These articles, most of which are to be contributed by guest authors, are intended to serve the readers of this JOURNAL *by calling attention to new developments in the theory, design, or availability of chemical laboratory instrumentation, or by presenting useful insights and explanations of topics that are of practical importance to those who use, or teach the use of, modern instrumentation and instrumental techniques.*

VIII. Instrumentation for Particle Size Analysis. Part Two

S. Z. Lewin, *Department of Chemistry, New York University*

The dispersal of the particles in a specimen, followed by the examination and measurement of each one individually, is generally considered to be the most unambiguous approach to the determination of the distribution of particle sizes in the sample, but even this technique is circumscribed by fundamental uncertainties. The limitation of the accuracy of discrete counting techniques stems not from the design of the instrumentation, but from the difficulty of selecting a representative sample and creating a thorough-going, stable dispersion of the particles in it without causing significant attrition, grinding, or other modification of the particles to occur in the process. As the preceding survey of instruments for discrete particle counting has shown, the accumulation of the numerical data can be achieved either by non-automated or fully automated techniques, the selection of the instrument design to be used in a given application being determined primarily by the relative availability to the user of time and personnel on the one hand, compared to money and laboratory space on the other.

Fractionation Techniques

The second approach to particle size analysis consists in the classification of the specimen into a number of fractions, each of which includes only particles whose dimensions fall within a limited range of values, followed by the determination of the weight or volume of these fractions. Two different means of implementing this approach are employed: (1) mechanical shaking of the specimen through a series of sieves having graded sizes of the sieve holes, and (2) utilization of the differences in the rates of sedimentation of particles having various sizes.

Sieves

A sieve consists of a suitable mounting for a sheet containing openings of uniform area, and in particle size analysis, a graded set of sieves is used in a stack, with the largest hole size at the top, and the smallest at the bottom. The specimen is placed in the top sieve, and the entire stack is closed by means of a cover on top, and a collector can at the bottom, as shown in Figure 11. The array of sieves is then shaken until the particles in the powder have had adequate opportunity to pass through those sieves the hole sizes of which exceed the smallest dimension of the particles. The stack of sieves may be held in the hands and shaken, or it may be mounted on a motor-driven table and shaken mechanically. An example of the latter type of device is the Fisher-Wheeler sieve shaker made by Fisher Scientific Co., Pittsburgh 19, Pennsylvania ($700), which is designed to give a combined vertical and horizontal rotation to the sample particles at a rate selectable in the range between 500 and 900 vibrations per minute. Other examples of mechanical sieve shakers are the Tyler Ro-Tap shaker available from Gardner Laboratory, Bethesda, Maryland, and LaPine Scientific Co., Chicago 29, Illinois ($600); and the Sieve Shaker and End-Shak machines made by American Instrument Co., Silver Spring, Maryland. A small, portable sieve shaker is available from LaPine Scientific Co. (hand-operated model $80; motor-driven model $112).

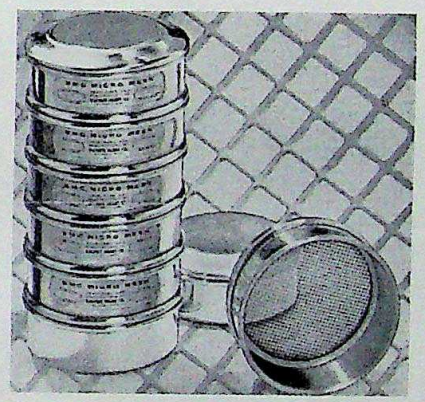


Figure 11. A standard sieve set for particle size analysis.

Sieves for particle size analysis are available with square holes, which is inevitable when they are made from wire screening, or round holes, which are produced by stamping, drilling, or etching sheet metal, and are available from most laboratory supply houses. An especially wide variety of sieves, including special designs, is available from the Buckbee Mears Co., St. Paul 1, Minnesota. The American Instrument Co. makes sieves for use in wet sieving experiments, where the solder used to hold a wire screen in its support would be corroded. These sieves have nickel-plated brass bodies and bronze screens, and the latter is held in the former by means of a bolted flange.

The hole sizes of wire mesh sieves are often designated in a number of different ways, several of which are sufficiently similar to represent a source of confusion and error to the unwary. The following tabulation shows the relationships among the most commonly used designations for wire mesh sieves. The Tyler series is designed so that an increase of two units in the mesh number corresponds to a decrease in hole size by the factor $1/\sqrt{2}$; this type of progression is convenient for the calculation of the particle size distribution from the measurement of the weights of the fractions retained by the various sieves.

Air Elutriation Fractionators

If air is blown through a powder at a controlled velocity, all particles smaller than a certain size (determined by the air velocity and the density of the substance) will be suspended in the air stream and can be floated away (or elutriated) from the

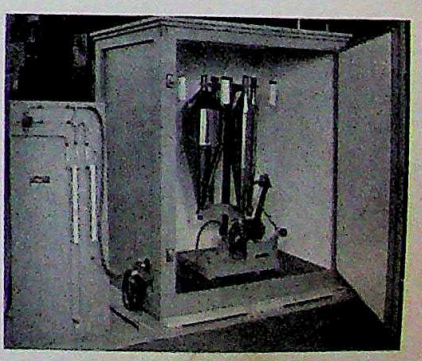


Figure 12. The Roller Particle Size Analyzer of the American Instrument Company.

(*Continued on page A350*)

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remainder of the specimen. This is the principle of the Roller Particle Size Analyzer made by the American Instrument Co. ($985). In this instrument, shown in Figure 12, the sample is placed in the bottom of a U-tube mounted below a settling chamber. Air passing into this U-tube stirs up the powder, as illustrated in Figure 13, and carries the lighter particles away and into the settling chamber, where opportunity is provided for the fractionation to be ameliorated due to the sedimentation of heavier particles. The light fraction passes up through the settling chamber and is caught in a paper thimble mounted at the end of a goose-neck tube on top of the settling chamber. The air stream passes out through the paper body of the thimble.

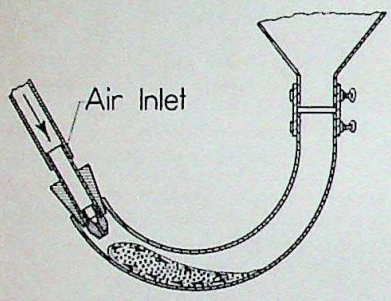


Figure 13. Diagram of the U-tube containing the sample in the Roller Analyzer.

U.S.A. sieve number	ASTM designation, microns	Tyler designation, mesh	Sieve opening In.	Sieve opening Mm.
4	4760	4	0.187	4.76
5	4000	5	0.157	4.00
6	3360	6	0.132	3.36
7	2830	7	0.111	2.83
8	2380	8	0.0937	2.38
10	2000	9	0.0787	2.00
12	1680	10	0.0661	1.68
14	1410	12	0.0555	1.41
16	1190	14	0.0469	1.19
18	1000	16	0.0394	1.00
20	841	20	0.0331	0.841
25	707	24	0.0278	0.707
30	595	28	0.0234	0.595
35	500	32	0.0197	0.500
40	420	35	0.0165	0.420
45	354	42	0.0139	0.354
50	297	48	0.0117	0.297
60	250	60	0.0098	0.250
70	210	65	0.0083	0.210
80	177	80	0.0070	0.177
100	149	100	0.0059	0.149
120	125	115	0.0049	0.125
140	105	150	0.0041	0.105
170	88	170	0.0035	0.088
200	74	200	0.0029	0.074
230	63	250	0.0025	0.063
270	53	270	0.0021	0.053
325	44	325	0.0017	0.044
400	37	400	0.0015	0.037

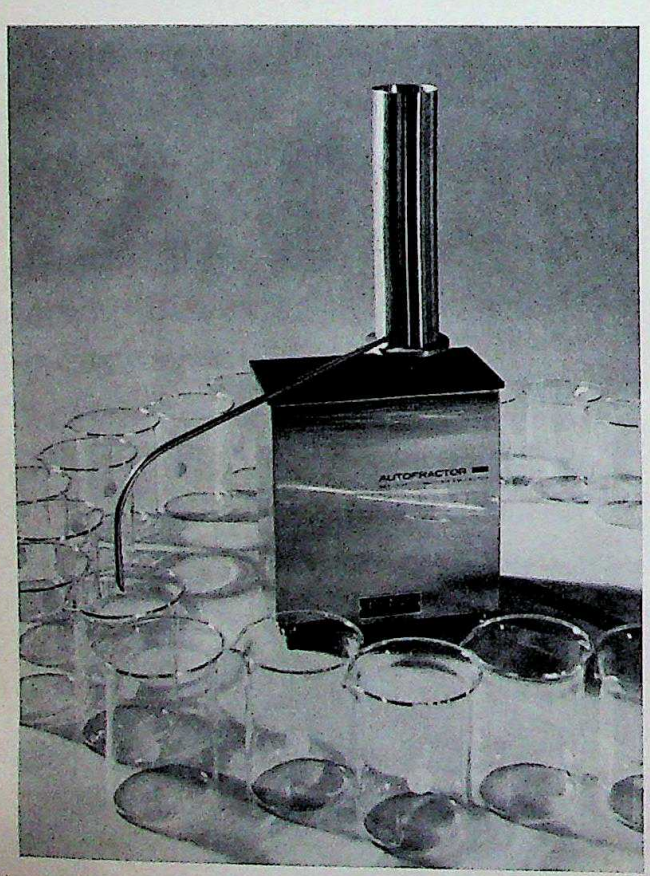
The relationship between the air flow rate needed to elutriate a particle of diameter d microns and having a density of ρ g/cm³, through a settling chamber of diameter D centimeters, is given by the formula:

$$F = 0.1409 \times 10^{-3} \rho d^2 D^2 \text{ liters/min.}$$

This is based upon Stokes' law for the rate of fall of a spherical particle through a viscous medium, taking the viscosity of the air in the apparatus as 1.82×10^{-4} poise, and neglecting the density of the air.

The U-tube is caused to oscillate at a rate of 200 times per minute under the action of leather-tipped fingers mounted on a motor-driven shaft, to keep the

(*Continued on page A352*)



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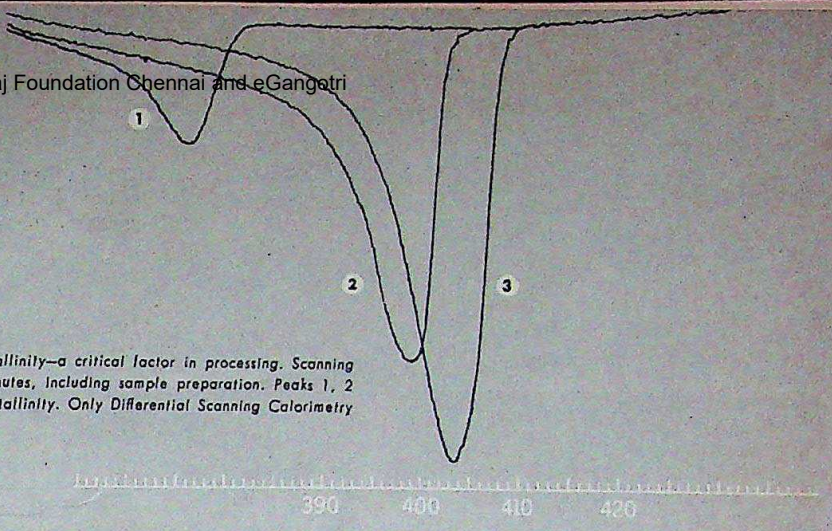
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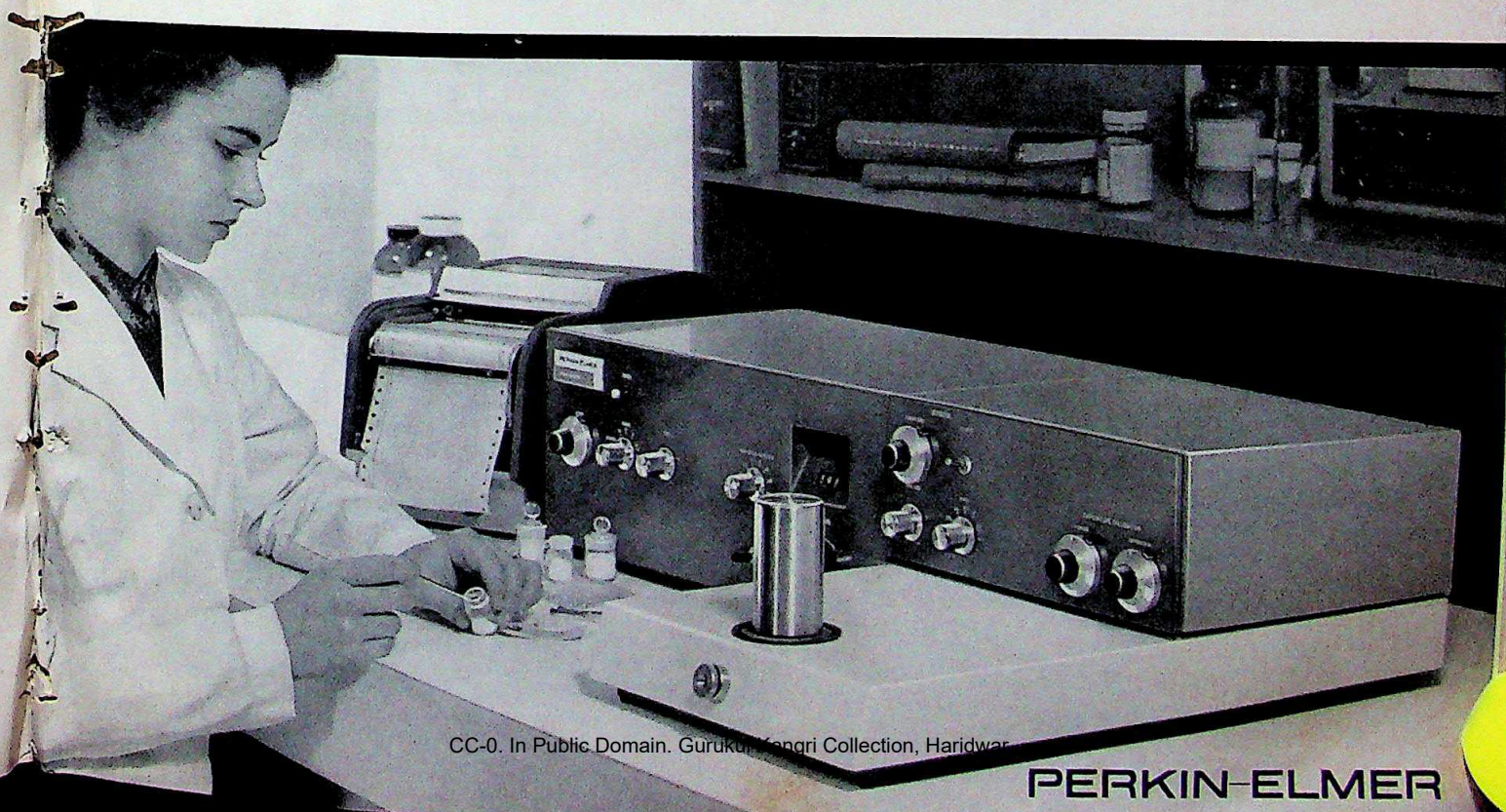
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sample stirred up and to aid in dispersing the lighter particles into the air stream. The cone of the settling chamber is tapped by a pair of hammers mounted on the motor-driven shaft, to help return the heavier particles to the U-tube. Four different settling chambers are provided, with diameters ranging from 1 to 9 inches, to be used in conjunction with different flow rates to yield different size fractions. This type of fractionator is useful for particles having diameters below about 80 microns. A typical series of fractions that can be collected by this equipment would be in the following order: 0–5, 5–10, 10–20, 20–40, and 40–80 microns, successively. The lighter fractions require 1 to 2 hours for collection; whereas the coarser size fractions may need only 10 to 30 minutes. About 20–30 grams of sample are usually employed for an analysis of this type.

An air elutriator in which the fractionation according to particle size is achieved by opposing the force of the air stream on the particles by a centrifugal force is the basis of the design of the Micro-Particle Classifier of Harry W. Dietert Co., Detroit 4, Michigan ($2900), shown in Figure 14.

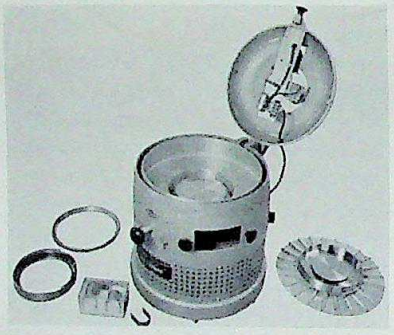


Figure 14. The Micro-Particle Classifier of H. W. Dietert Co. Centrifuge is in center; rotating fan is at right.

The design principle is illustrated in Figure 15. Rotation of the fan wheel in the centrifuge assembly of the rotor casting creates a spiral of air that comes from the extremity of the rotor casting and is driven in toward the center axis through the sifting chamber. The sample is introduced through a hopper, where it is shaken mechanically and dispersed by means of a bristle brush into the air stream. As the sample enters the air stream, it feels a centrifugal force tending to drive it toward the periphery of the apparatus, while the air flow tends to drive it toward the center. Thus, the dispersed sample entering the sifting chamber is separated into a light fraction and a residue. The light fraction is carried by the spiral of air out through the fan and is deposited inside the upper rotor casting. The remaining heavier portion of the sample is driven by centrifugal force against the air flow and is deposited as a uniform drift on the inside wall of the sifting chamber. The difference in weight between the total

(Continued on page A354)

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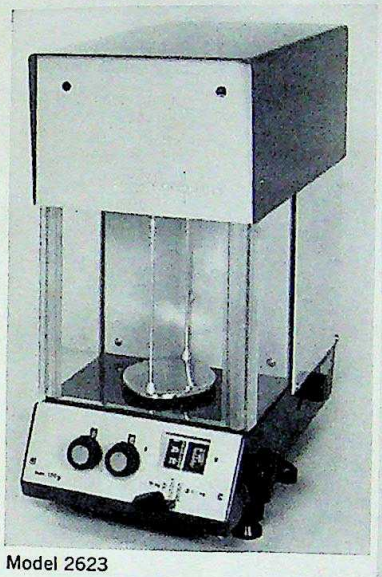
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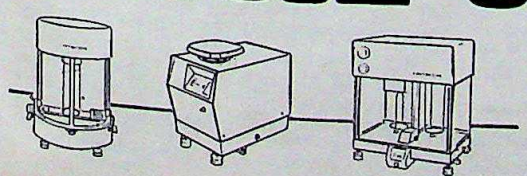


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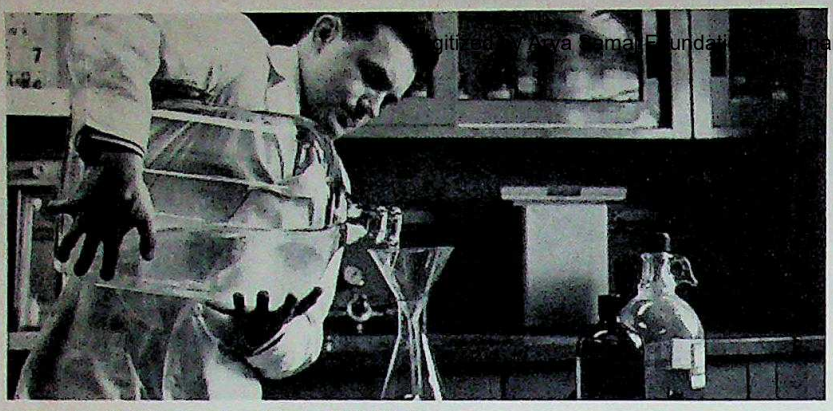
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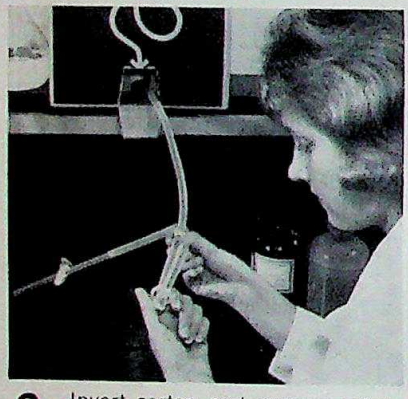
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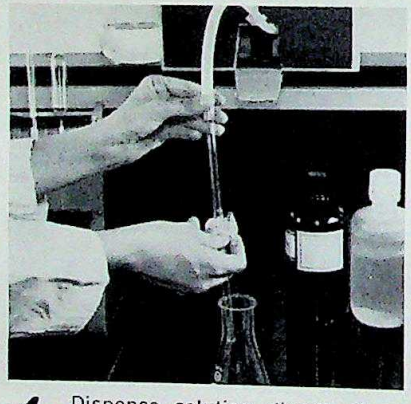
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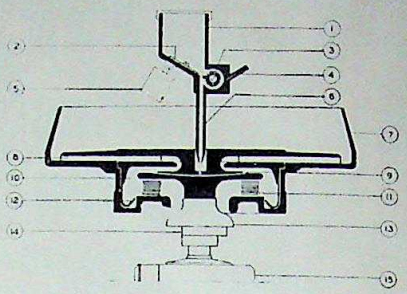


Figure 15. Diagram of the design principle of the Dietert Micro-Particle Classifier: 1, hopper; 2, spring plate; 3, brush; 4, orifice tube; 5, vibrator; 6, feed nozzle; 7, rotor casting; 8, fan wheel vanes; 9, rotary duct opening; 10, sifting chamber; 11, symmetrical discs; 12, catch basin; 13, throttle nut; 14, throttle spacer; and 15, motor.

sample introduced and the residue retained in the catch basin is used to determine the weight of the light fraction. This procedure is then repeated, using the residue from the previous run as the new sample to be introduced, and employing a different size of the air inlet to allow a coarser particle fraction to be elutriated. Each run (i.e., fraction collected) requires about 15 minutes, and as many as 8 fractions can be obtained with the throttle spacers provided with the instrument. The amount of sample employed is 10–20 grams, and the working range is 0–60 microns.

Sedimentation Balances

An alternative application of the principle that the rate of settling of a particle suspended in a fluid is a function of its size is found in the sedimentation balance. Stokes' law may be written in the following form:

$$T = \frac{9\,\eta\,H}{2\,g\,(\rho_1 - \rho_2)}\,\frac{1}{r^2}$$

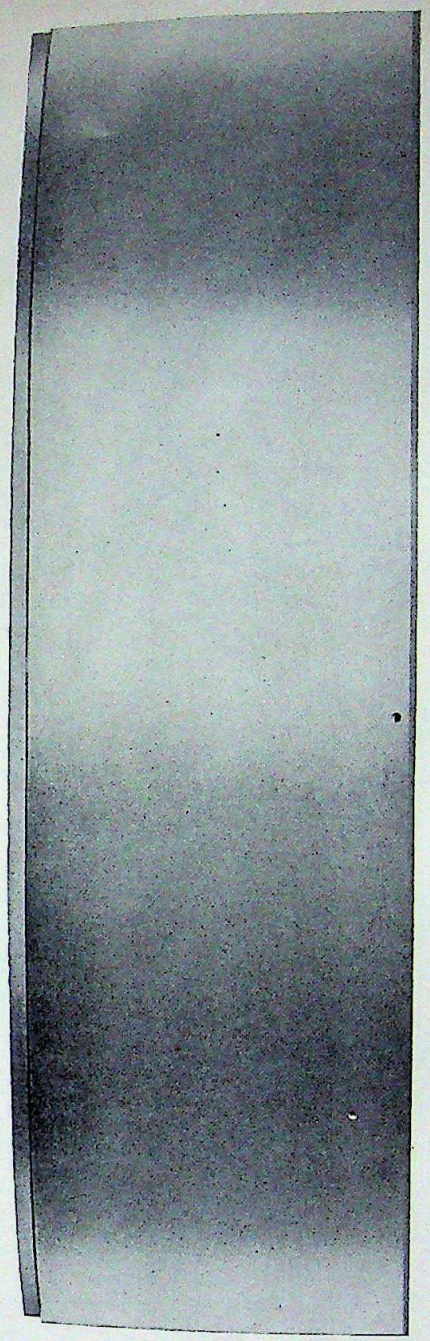
where T is the time required for a particle of radius r and density ρ_1 to fall a distance H through a fluid of viscosity η and density ρ_2. Hence, if a specimen is thoroughly dispersed in a fluid, and if a balance pan is placed near the bottom of this suspension, the increase in the weight on the pan that occurs during specific time intervals will measure the quantity of particles of various size range, the coarsest particles settling out in the shortest time, and the finest particles requiring the longest times.

The Sharples Micromerograph made by Franklin Electronics, Inc., Bridgeport, Pennsylvania, shown in Figure 16, is a sedimentation balance in which a servo-controlled, continuous-recording, null-balance instrument weighs the sediment as a function of time, and draws a graph of the results. The settling chamber is an extruded aluminum tube, $3\frac{1}{2}$ inches in inside diameter and 85 inches long, and is covered with a Fiberglass blanket to

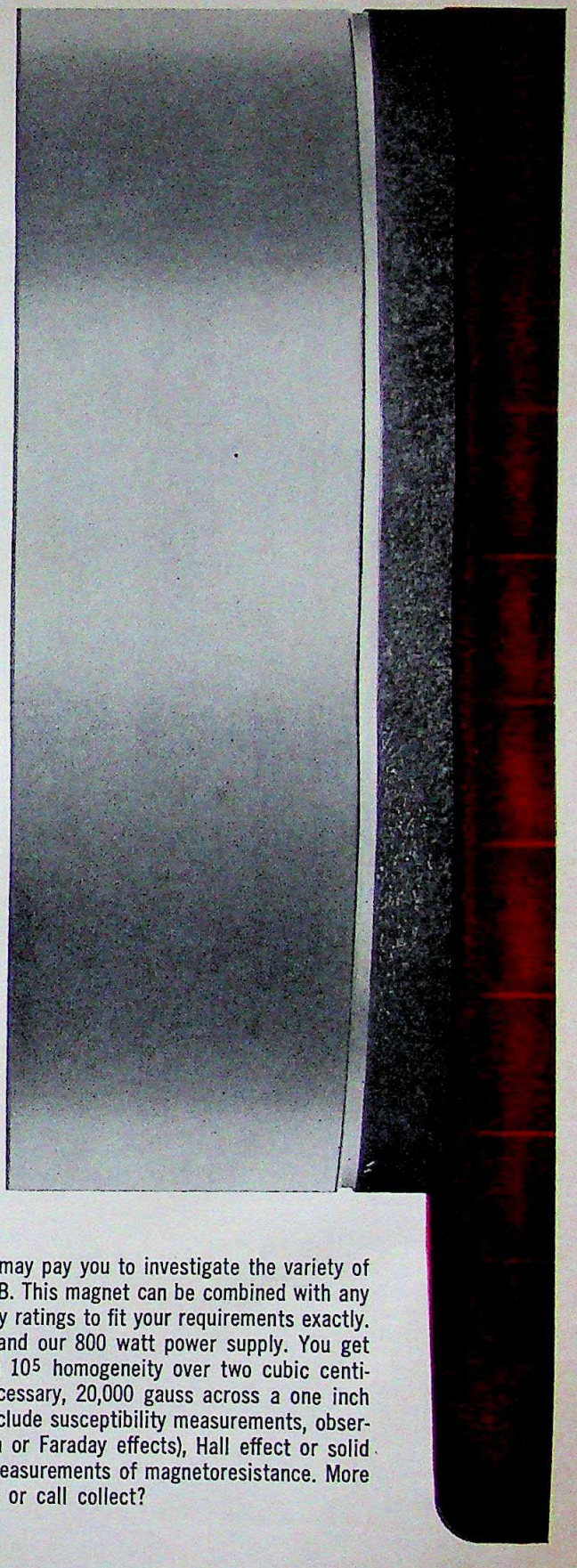
(*Continued on page A356*)

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EPR



If you are planning work involving precision electromagnets it may pay you to investigate the variety of systems available which use the seven inch magnet Model L-75B. This magnet can be combined with any of four different power supplies with various output and stability ratings to fit your requirements exactly. For "X" band EPR choose the gap shown above (actual size) and our 800 watt power supply. You get necessary field strength — 3,000 to 4,000 gauss, one part in 10^5 homogeneity over two cubic centimeters, for less than $5,000. If higher field strengths are necessary, 20,000 gauss across a one inch gap can be obtained using a 5 KW power supply. Other uses include susceptibility measurements, observation or illumination of the sample along the H axis (Zeeman or Faraday effects), Hall effect or solid state studies, broad line NMR, low temperature studies, and measurements of magnetoresistance. More performance and applications data is available. Why not write or call collect?

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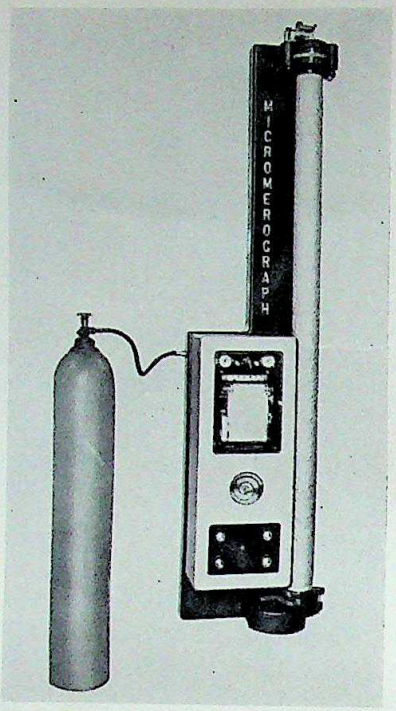


Figure 16. The Sharples Micromerograph of Franklin Electronics. Settling tube is at right; servo-controlled balance is at base of settling tube, and electronics is in central box. Gas cylinder at left is for providing a burst of gas to suspend sample particles.

provide thermal insulation. The sample used is about 0.1 g in amount, and the range of particle sizes that can be determined is 0–250 microns. The particles settle through air, and the sample is introduced into the settling chamber by releasing a charge of nitrogen gas through the sample in order to deagglomerate it while suspending it.

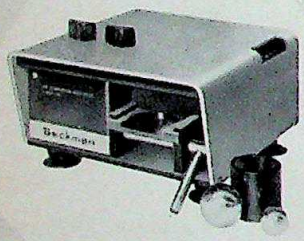
The Gallenkamp Particle Size Determination Apparatus ($850), available from Arthur S. LaPine and Co., Chicago 29, Illinois, is a sedimentation balance for liquid suspensions, employing a direct-reading torsion balance. The range of particle sizes most appropriate for this instrument is 5–75 microns.

The Micron Particle Distributometer made by G. F. Bush Associates, Princeton, New Jersey, is a sedimentation balance for liquid suspensions utilizing an electrical sensing balance with a sensitivity of 30 microamperes per milligram, that can be used to provide a signal for a standard graphic recorder.

An example of a step-recording sedimentation balance is the Sedimentograph made by Shimadzu Seisakusho Ltd., Tokyo, and shown in schematic diagram in Figure 17. When a given weight of sediment has accumulated on the balance pan, the beam deflects enough to make contact with a pair of solenoid contacts, actuating a relay which causes a steel ball to be released and fall on the other pan, thereby restoring the balance beam to its null position. This action simultaneously

(*Continued on page A358*)

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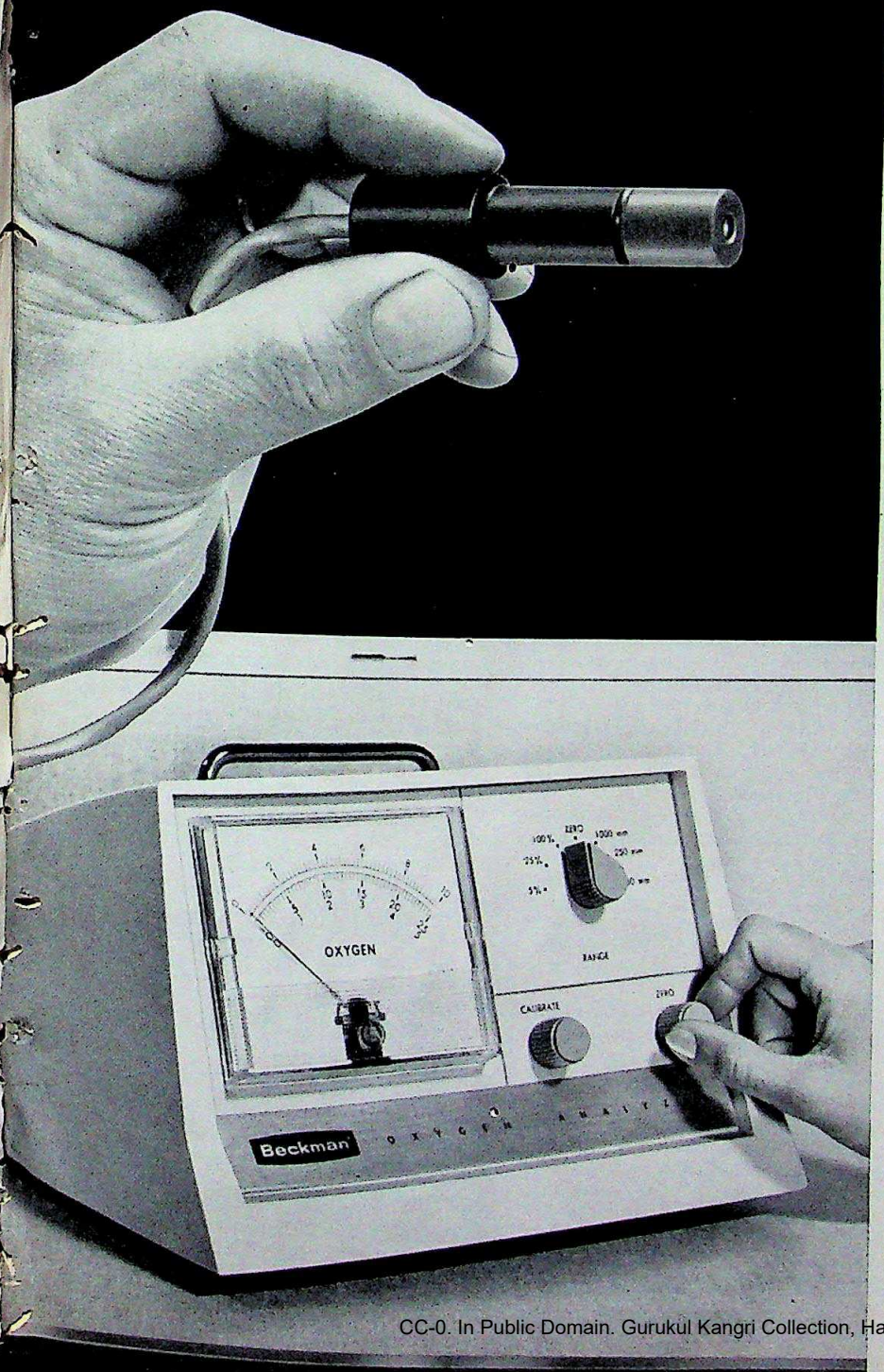
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Beckman Oxygen Adapter allows the Beckman Model 76 Expanded Scale pH Meter to function as an oxygen analyzer. The Model 76 can then provide the same oxygen measurement ranges as the Model 777 with the same accuracy. The laboratory is thus equipped with a multi-purpose instrument readily convertible for either pH or oxygen measurements.

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causes a pen to be displaced on a chart, and thus the weight of the sediment is recorded in step increments as a function of equal

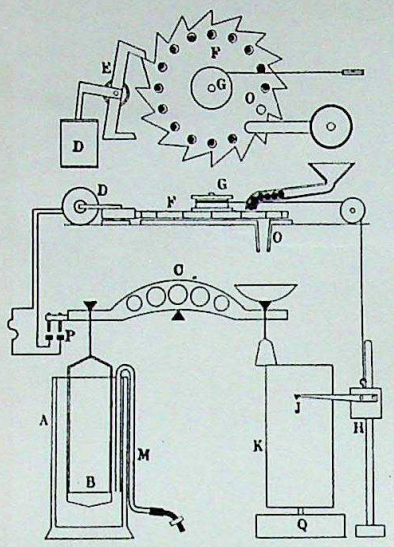


Figure 17. Schematic diagram of the design principle of the Sedimentograph: A, sedimentation bottle; B, balance pan on which the powder settles; C, balance; P, contact point of electric current; D, electric magnet; E, ratchet; F, rotating plate; G, pulley; H, sliding weight; J, pen; K, recording drum; Q, clock for rotating the drum; and M, siphon.

time increments. The areas under segments of the chart record corresponding to equal weight increments can be used to develop the particle size distribution curve, as illustrated in Figure 18.

Sedimentation Volumenometers

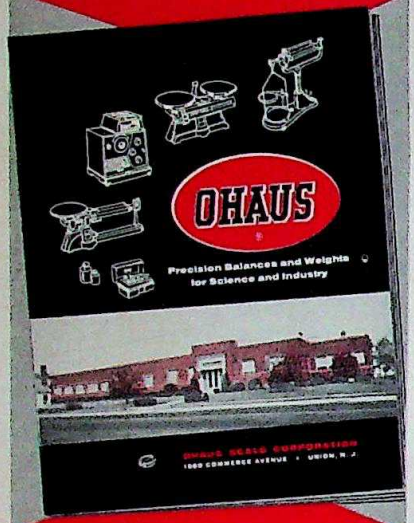
Instrumentation has also been designed on the principle that the volume of sediment formed in a given time interval may be related to the sizes of the suspended particles which pack together into that sediment. The simplest of these devices is nothing more than a settling tube with a graduated receiver at its lower end. An example of this type of device is the Palo-Travis Particle Size Apparatus of Palo Laboratory Supplies, Inc., New York 7, New York ($82.50). It consists of a jacketed settling tube coupled to a calibrated collecting tube by means of a large-bore stopcock. The particle size range for which this device is designed is 2–44 microns.

Sediment volumes tend to be sensitive to many factors in addition to the particle size distribution, and for this reason, sedimentation volumenometers should be calibrated for the specific substances of interest under the same conditions of use.

In order to improve the reproducibility of packing of the sediment and thus improve the precision of the volumetric approach to particle size analysis, the Mine Safety Appliance Co., Pittsburgh 8, Pennsylvania, has developed a volumenometer that utilizes a controlled centrifu-

(Continued on page A360)

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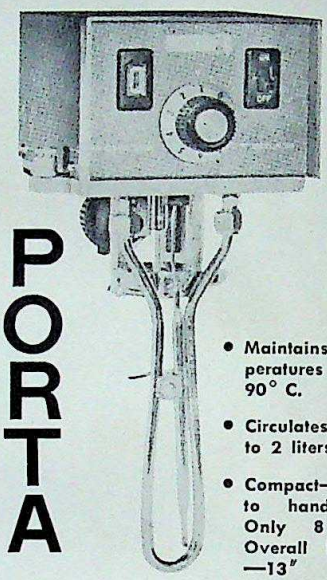
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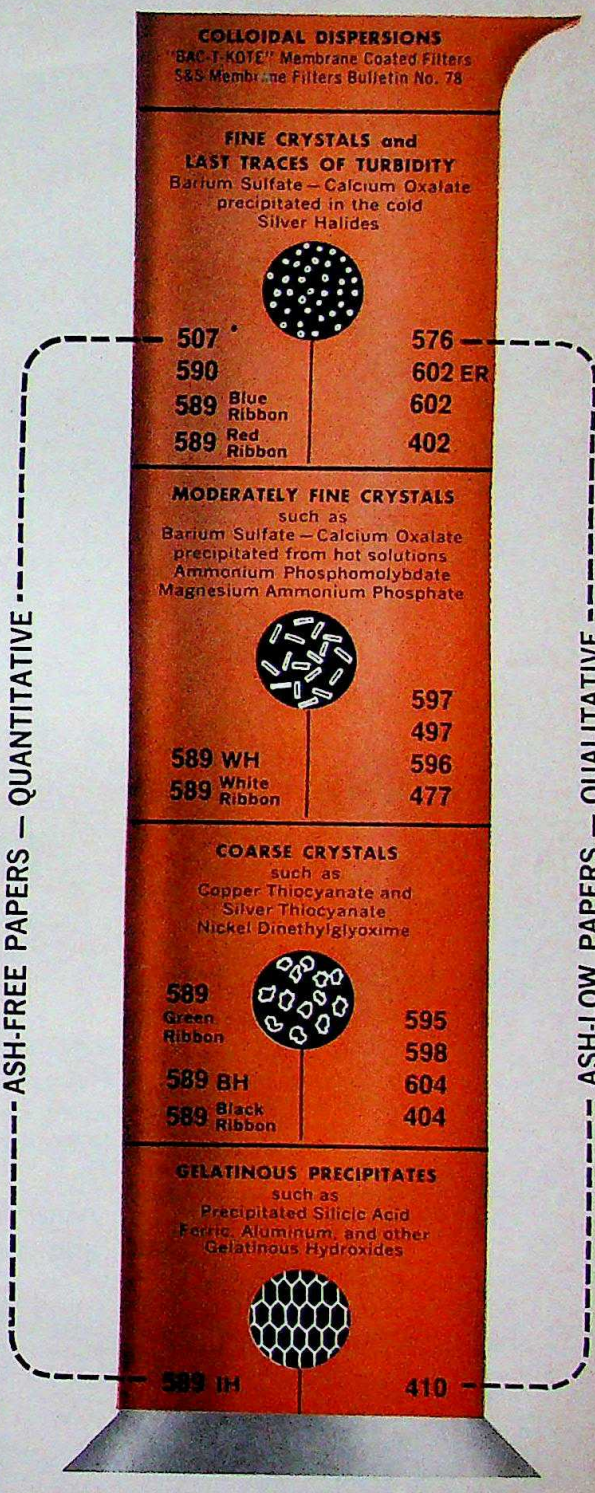
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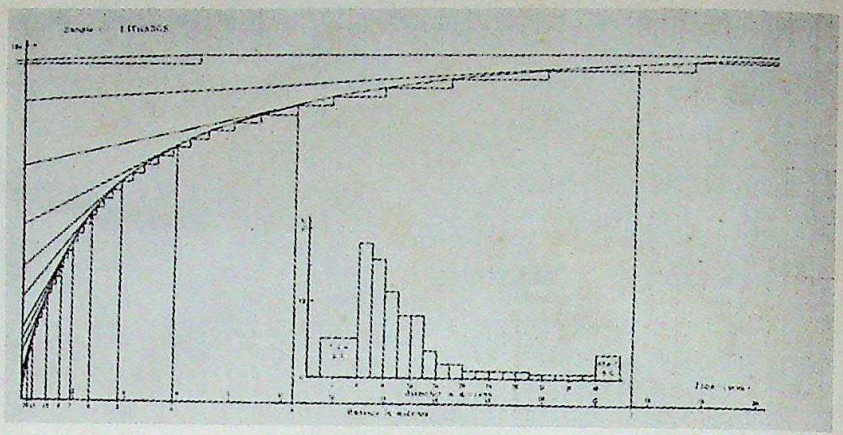


Figure 18. Form of read-out data generated by the Sedimentograph at left, with derived particle size distribution shown in center.

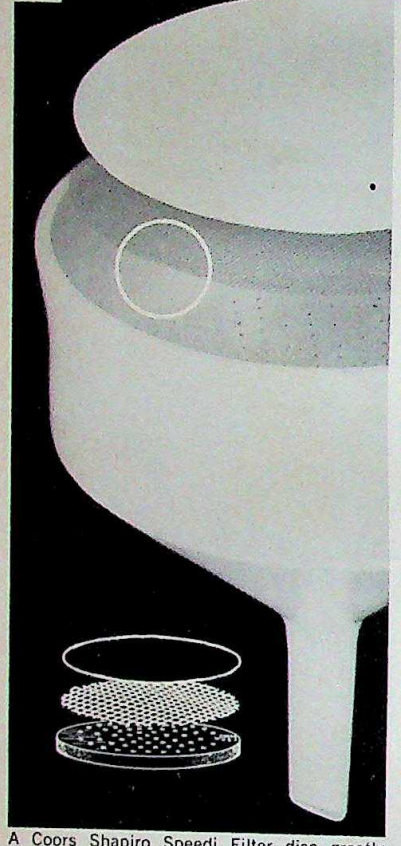
gal force as the motive agent (MSA Particle Size Analyzer, centrifuges $500 each, projector-reader $500). The two basic units of this instrument are shown in Figure 19.

The sample is deagglomerated and suspended in a suitable liquid medium, and this is transferred to form a layer on top of a standard volume of the sedimentation liquid in a centrifuge tube. The tube is placed in a centrifuge, where it is rotated for a fixed time at a constant speed, after which it is removed from the centrifuge, inserted in the projector, and the height of the sediment is read. The tube is then returned to the centrifuge for further sedimentation; the particle size distribution is finally deduced from the variation of sediment height as a function of the total duration of centrifugation.

The centrifuges designed for this application are constant speed, controlled acceleration and deceleration units, with a built-in timer, buzzer, and switch. Three different centrifuges are available, providing 300, 600/1200, and 1800 rpm, respectively. These are particularly suit-

(*Continued on page A364*)

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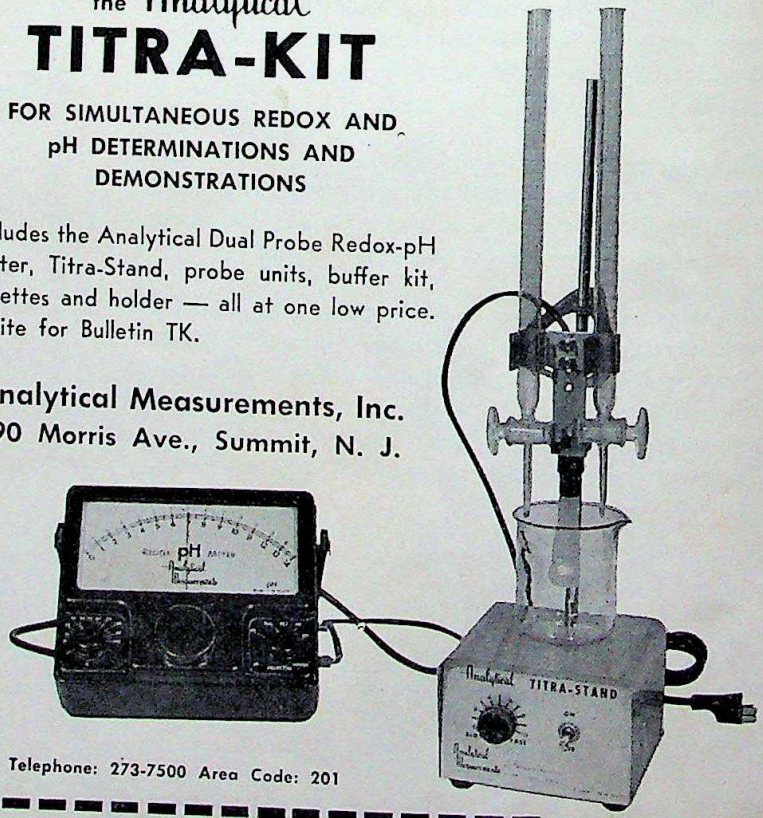
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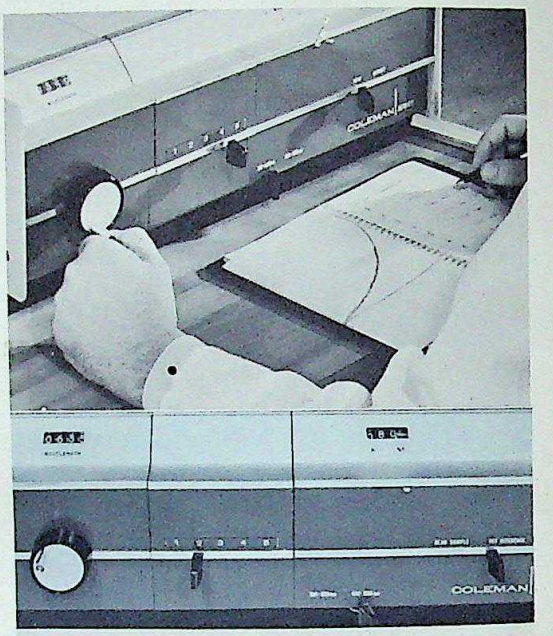
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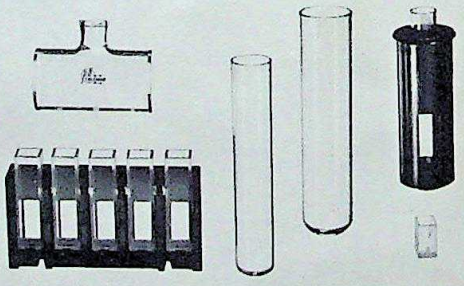
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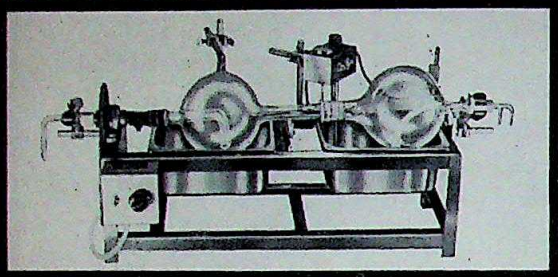
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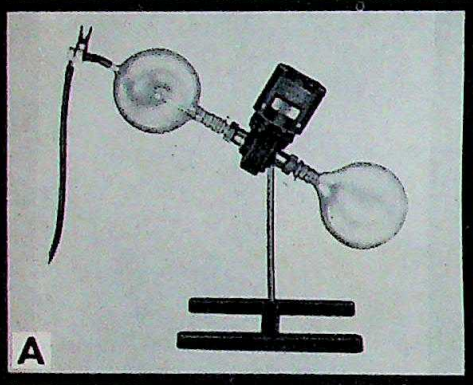
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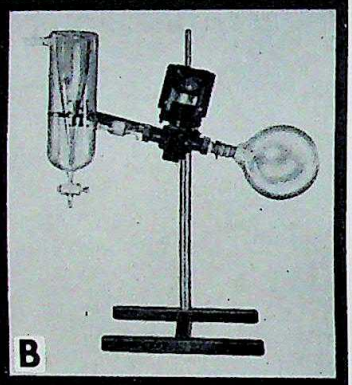
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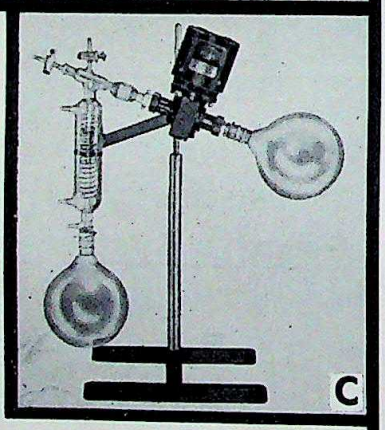
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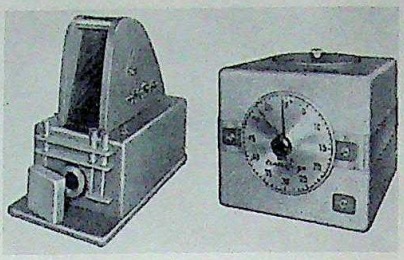


Figure 19. Basic units of the MSA Particle Size Analyzer. The centrifuge unit is shown at right, and the projector-reader is at left.

able for particle size ranges of 10–30, 2–10, and 0.1–1 microns, respectively.

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Next: Conclusion of the survey of instrumentation for the determination of particle size

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Mettler

METTLER H-6 SPECIFICATIONS

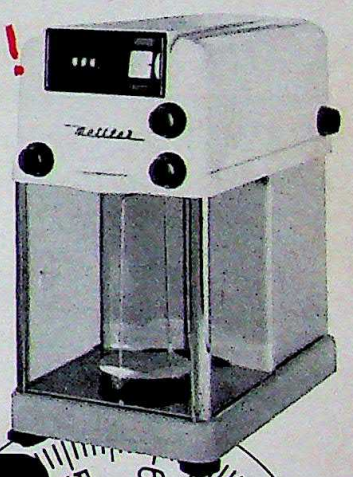
PERFORMANCE DATA	
Capacity	160 g
Optical Scale Range	1200 mg
Sensitivity (1 micrometer graduation)	0.1 mg
Readability (1 micrometer graduation)	0.1 mg
Accuracy of weight set	± 0.1 mg
Accuracy of weighings within optical range	± 0.1 mg
Precision	± 0.05 mg

DESIGN DATA	
Damping	differential, top and bottom air damping
Knife edges and planes	synthetic sapphire
Taring range (up to)	15 g
Pan:	chrome-nickel steel
diameter	3½"
bracket height	6½"
Weights, annular	non-magnetic chrome-nickel steel
*Density	7.77 g/cm^3
Housing	plastic, two colored
Base Plate	light alloy
Dimensions: width	8-3/4"
depth	14"
height	15½"
Voltages	4 settings, from 110 to 220 V AC, set for 110
Net weight	17.5 lbs
Shipping Weight	24 lbs

ACCESSORIES: Adaptor, Screwdriver, Dust brush, Cleaning cloth, Dust cover, Spare bulb.

*) at air-density 1200 mg/l calibrated to apparent mass of density 8.4 g/cm^3.

H-6



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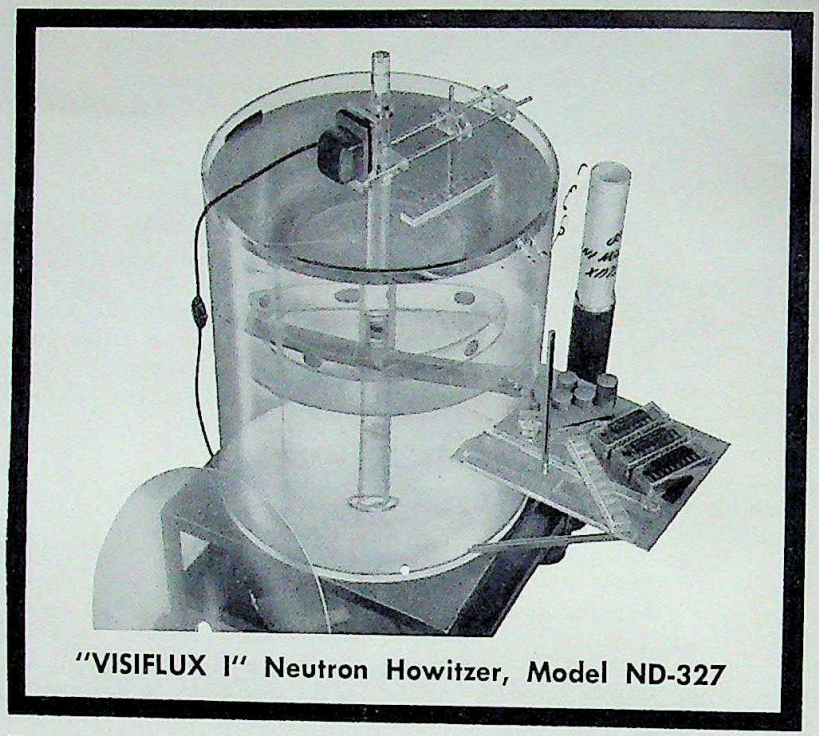
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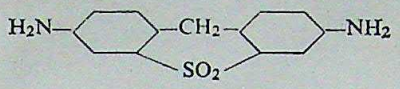
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NO_2^- or no . . . Mr. Gibson's pictures

Stein's baby

Dissatisfied with ordinary reagents for nitrite ion? O. Stein suggests



and remarks:

> "A characteristic of this new sulfone is its enormous affinity for nitrous acid. In a water solution of hydrochloric acid, the smallest amount of nitrous acid produces an intense blue coloration . . . even greater than that formed by m-phenylenediamine. This reaction which takes place with nitrous acid does not take place with diazo compounds. Certainly, perhaps [he puts it *sichert ihm vielleicht*], it has an application as an indicator for the titration of aromatic amines with sodium nitrite."

Certainly perhaps you should delay no longer in taking him up on it, since his suggestion is already 69 years old (*Ber.*, *27*, 2806) and we have at last gotten around to following out his directions for preparation. Thus we can offer the reagent as EASTMAN 8776. Directions for use until you improve on them: Make 10% solution in dilute HCl. Place a few drops on filter paper. Add one drop of solution under test. An unstable blue color indicates NO_2^-. Somewhat less sensitive than starch-iodide but works even in strongly acid solution. These directions come from the celebrated Fierz-David "Künstliche Organische Farbstoffe," available in an English translation by Paul W. Vittum* (Interscience Publishers, Inc., New York, 1949).

EASTMAN 8776 (5 g., $2.70; 25 g., $9.60) comes labeled *3,7-Thiaxanthenediamine-5,5-dioxide*. Stein would never have recognized his baby under that name. Vittum's translation calls the compound "4,4′-diaminodiphenylmethane-2,2′-sulfone." Ladies and gentlemen, organic nomenclature is for practical purposes **a little bit of a mess . . .**

so . . .

A new edition, No. 2F, of "Eastman Organic Chemicals Classified by Functional Groups" has just gone out to the mailing list for our catalog. We do not kid ourselves or you. It contains no magic that allows a person to select organic chemicals without troubling to acquire a proper chemical education.† It does offer much to one who knows a little about the *Chemical Abstracts* nomenclature we use. He needn't be such a whiz that he could at once translate the structural formula on this page into the proper chemical word-designation to look up alphabetically among the 4100 entries in "Eastman Organic Chemicals List No. 43." He *would* have to know the name when he sees it in a list of 55 "AMINES, Aromatic, Polyamines." Alternatively, he might have found it among the 67 "HETEROCYCLIC COMPOUNDS, Sulfur," or the 11 "SULFUR COMPOUNDS, Sulfones and Sulfoxides."

Our little book also has another mode of use. Suppose you go into it asking, "What's readily available these days in AMIDES, CARBOXYLIC, Aromatic?" Quickly you learn from which 23 such you can take your pick. Want it with a naphthalene structure and a hydroxyl group? We offer 65 "HYDROXYL COMPOUNDS, Ring, Naphthalene." Intersection: *3-Hydroxy-2′,4′-dimethyl-2-naphthanilide* (EASTMAN T7259). Bingo!

If you haven't received a copy yet and need one, let us know. If you don't even have "Eastman Organic Chemicals List No. 43" you *are* in trouble, but the pain can be alleviated by Distillation Products Industries, Rochester 3, N. Y. (Division of Eastman Kodak Company).

Prices subject to change without notice.

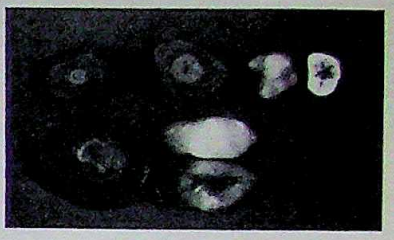
*Having done his bit to dredge up various goodies for the general benefit of mankind from the depths of the dye chemist's black and other-colored art, Dr. Vittum keeps busier these days managing Kodak's color photography research.

†If this sounds as though we don't want to sell EASTMAN Organic Chemicals to individuals without professional training, you read it right.

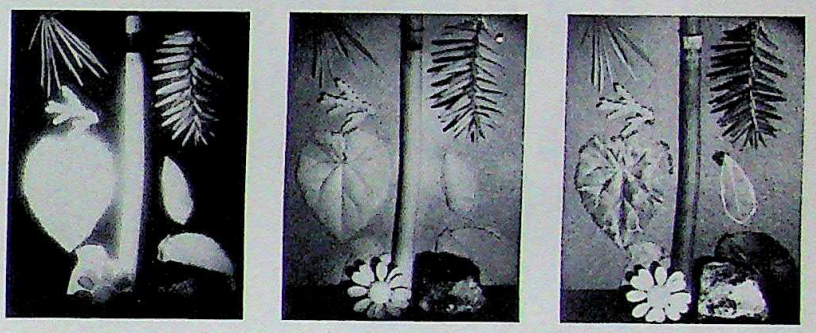
Fluorescence in the infrared



Here is an ordinary photograph of gallstones



and here they are by fluorescence in the near infrared.



Here are an assortment of plant fragments and a chunk of greenockite by infrared fluorescence, infrared reflection, and visible.

Illumination for the fluorescence shots was blue-green light with all the infrared filtered out. In front of the KODAK RETINA Reflex Camera loaded with KODAK High Speed Infrared Film, a KODAK WRATTEN No. 87 Filter passed only radiation longer than 740mμ. To record infrared reflection instead of infrared fluorescence, we removed the blue-green-passing, infrared-absorbing filter from the lamp, left everything else the same, and cut exposure time 20,000 times.

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This is another advertisement where Eastman Kodak Company probes at random for mutual interests and occasionally a little revenue from those whose work has something to do with science

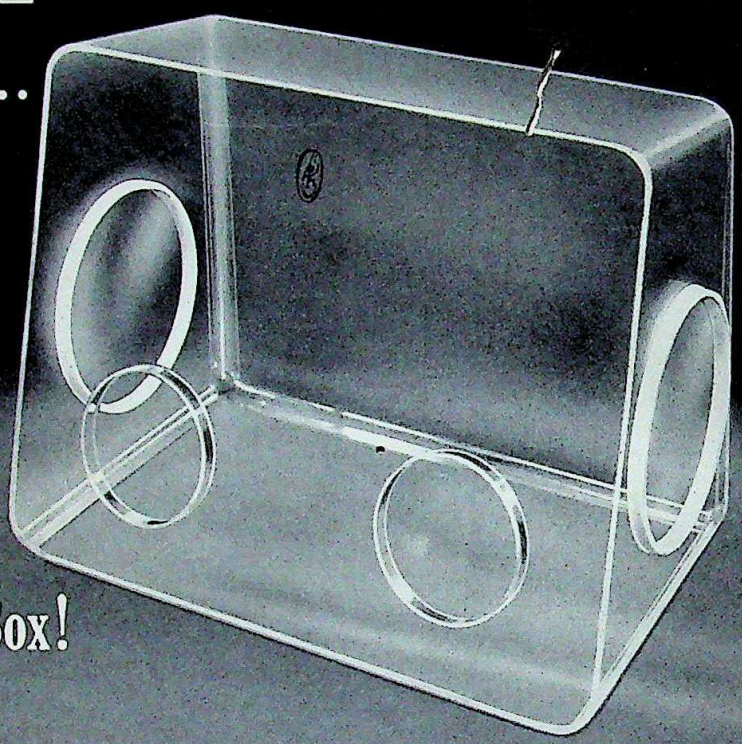
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Chem Ed

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Edited by William G. Kessel

When writing for additional information about new products or for new literature, your inquiry will receive prompt attention if you write on your firm or institution letterhead and mention the Journal of Chemical Education and the date of the particular issue. Pamphlets, booklets and similar literature are gratis unless otherwise specified.

New Apparatus and Equipment

▶ A new scaler-ratemeter, Model SR-234, that doubles as a low-cost teaching aid and a general laboratory monitor, is now available from Atomic Accessories Inc., 811 W. Merrick Rd., Valley Stream, L. I., New York.

▶ A solid state variable power source with manual selection of voltage from 0–60 v, the Un-A-Watt, is presently available from Kontes Glass Co., 126 Spruce St., Vineland, New Jersey.

▶ Phoenix Precision Instrument Co., 3883-05 N. Fifth St., Philadelphia 40, Pennsylvania, announces the availability of a new reusable device for vacuum hydrolysis. The newly designed, reusable vacuum hydrolysis tube is a unique apparatus that is useful for the hydrolysis of proteins and other polymeric materials, which must be handled in an inert atmosphere.

▶ F and M Scientific Corp., Route 41 and Starr Rd., Avondale, Pennsylvania announces the addition of the Model 180 carbon, hydrogen, nitrogen analyzer to its line of analytical instrumentation. This new instrument permits the accurate, rapid and simultaneous determination of these elements in a single analytical procedure.

▶ Lightweight portable "Lab Towers" that substantially increase rack area by as much as 350% without any subsequent increase in or loss of floor space, is the latest addition to the "Portable Systems" line offered by Penn-Chem Corp. of Lancaster, Pennsylvania.

▶ The Loenco single or dual hydrogen flame ionization detectors, in conjunction with the Model 21B electrometer, make a gas chromatographic quantitative analysis of organic compounds in parts per billion possible. For complete information of these detectors and electrometer write for *Data Sheet LOE-10*. Loenco, Inc., 2092 N. Lincoln Ave., Altadena, California.

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▶ The first direct reading spectrophotometer, Model 139 UV-VIS, which employs a precision diffraction grating to cover the entire ultraviolet and visible region has been announced by the Perkin Elmer Corp., Norwalk, Connecticut.

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▶ Nuclear Magnetic Resonance Specialties, 145 Greensburg Rd., New Kensington, Pennsylvania, a two-year-old firm manufacturing accessory instrumentation for analytical nuclear magnetic resonance spectrometers, has announced that it is now prepared to perform NMR analytical services on a commercial basis.

▶ Philadelphia Scientific Glass Co., Inc., Perkasie, Pennsylvania, has developed an extremely small, $1/2 \times 1/10$ in., and lightweight thermostat which is ideal for aerospace or other applications where minimum size and weight are essential.

▶ A new, economical, all rubber vacuum valve has just been introduced by Thermo-

(*Continued on page A371*)



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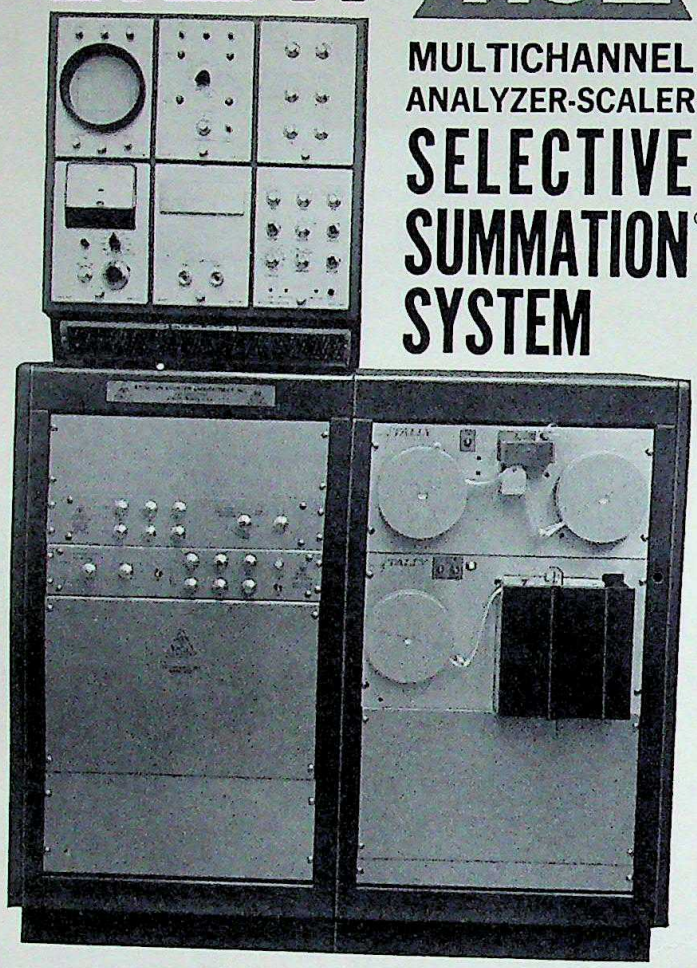
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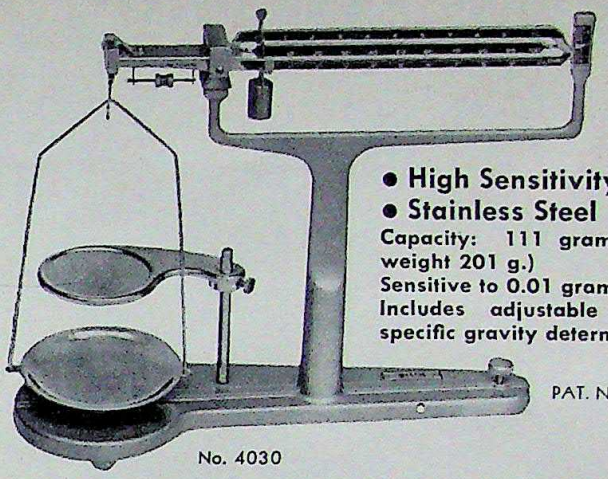
▶ The HR-97 is a high performance 11 × 17 in. X-Y recorder which has 1 mv/in. basic sensitivity, 0.25% of full scale accuracy, 15 in./sec pen speed, zener reference voltages, snap-on pen assembly and vacuum paper holddown. Write Houston Instrument Co., P.O. Box 22234, Houston 27, Texas for details.

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(*Continued on page A372*)

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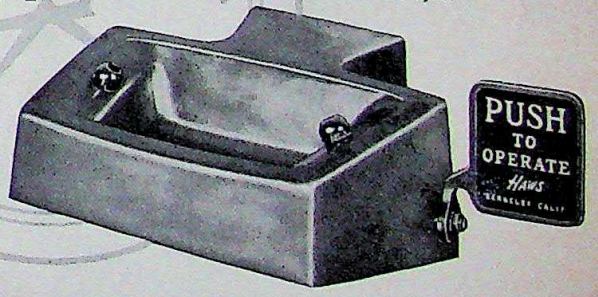
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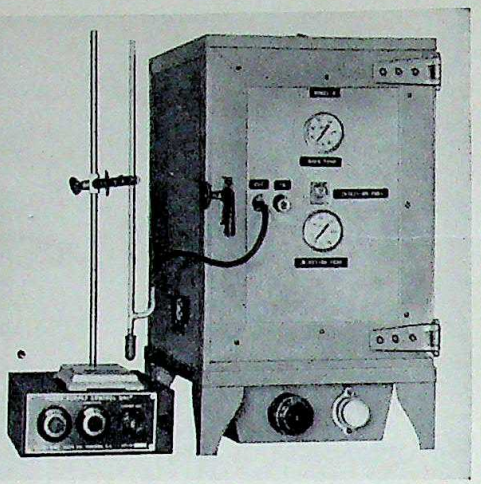
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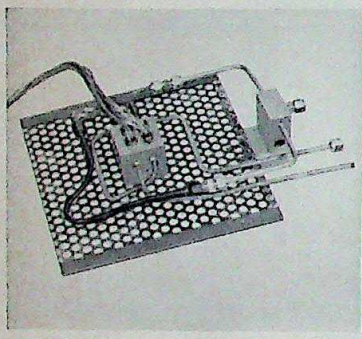
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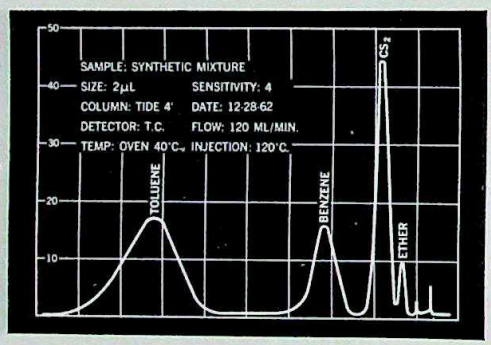
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GAS ANALYSIS INSTRUMENTS SINCE 1935

Out of the EDITOR'S BASKET

CD-412, *New Opportunities with Phenolics,* available now from the Chemical Materials Dept. of General Electric Co., One Plastics Ave., Pittsfield, Massachusetts.

● Gallard-Schlesinger Chemical Mfg. Corp., 1001 Franklin Ave., Garden City, L. I., New York offers a new loose-leaf catalogue covering compounds which are of pure research interest, a few analytical chemicals and between 10 and 20% inorganic materials.

● Twenty-five products designed to save space, eliminate breakage and generally simplify laboratory procedures are contained in a new 4-page, 2-color brochure just issued by Penn-Chem. Corp., 232 N. Marshall St., Lancaster, Pennsylvania.

● Alpha Scientific Laboratories, P.O. Box 333, Berkeley 1, California offers a 16 page booklet on the theory of (ESR) Electron Spin Resonance.

● A laboratory service fixtures guide for specification writers involved with educational, medical and industrial laboratories, is now being distributed by T&S Brass and Bronze Works, Inc., 128 Magnolia Ave., L. I., N. Y., manufacturers of Lab-Flo laboratory service fixtures.

● F.&M. Scientific Corp., Avondale, Pennsylvania has published and has available reprints of a paper entitled *Analytical Applications of Dual Column Gas Chromatography* by Louis Mikkelsen, J. V. Wisniewski and M. G. Beck. Presented at the Southwestern Regional Meeting of the ACS in Dallas, Texas in December, 1962 by M. G. Beck, the paper discusses some parameters required for column compensation and the quantitative efficacy of the technique.

● Bethlehem Apparatus Heathway Sales Co., Front and Depot Sts. Hellertown, Pennsylvania offers *Catalogue No. 61-A* describing a new and unique glass lathe which may be used in either the horizontal or vertical position permitting operations impossible or unusually difficult to accomplish with the conventional horizontal lathe.

● Cahn Instrument Co., 15505 Minnesota Ave., Paramount, offers a reprint list describing work done and publications available in pharmaceutical chemistry, food processing, histochemistry, electronics, vacuum weighing, air pollution, contamination analysis and micro sample handlings.

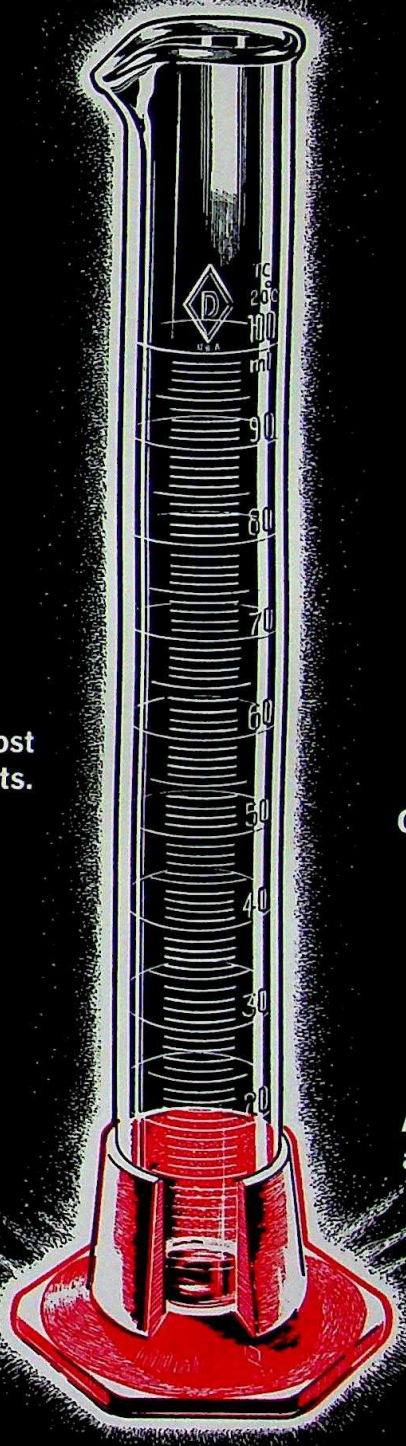
● A symposium of 25 factual reports, by laboratory directors who have instituted automatic glassware washing programs within the past two years, has been published by the Facilities Planning Dept. of The Chemical Rubber Co., 2310 Superior Ave., Cleveland 14, Ohio.

(*Continued on page A374*)

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● Electric desalters, sample applicators and the "Chromatobox" are described in *Aids to Chromatography* issue of the *RSCo Review*, Volume 4 No. 7. Write Research Specialties Co., 200 S. Garrard Blvd., Richmond, California.

● Perkin Elmer Corp., 1001 Main Ave., Norwalk, Connecticut, offers *Fatty Acids Analysis* and *Gas Lasers* on request.

● A technical paper on instruments for neutron health monitoring is available from Texas Nuclear Corp., 359 E. Howard Ave., Des Plaines, Illinois. Ask for *Neutron Topics No. 3.*

● *Carbon Dioxide as an Agent in Chemical Energy* contains a detailed description of the Oak Ridge, Tennessee, and Paducah, Kentucky, nuclear facilities, which Union Carbide operates for the U.S. Atomic Energy Commission. Write for a copy to Public Relations Dept., Union Carbide Corp., 270 Park Ave., New York 17, N. Y.

● A new 12-page engineering catalogue dealing with "Vulcathene" non-corrosive plastic drainlines has been released by Nalgene Piping Systems, Division of The Nalge Co., Inc., 75 Panorama Creek Dr., Rochester 2, New York.

● Beckman Instruments, Inc., Scientific and Process Instruments Division, 2500 Harbor Blvd., Fullerton, California, announces publication of a 50-page literature packet describing all accessories for Beckman Infrared Spectrophotometers.

● *Contamination Control*, which was prepared for technical personnel, is available from the Bell Telephone Laboratories, Holmdel, New Jersey.

● Ultra-Violet Products, Inc., 5114 Walnut Grove Ave., San Gabriel offers for 50 cents a booklet, *Black Light and Fluorescence*, as well as free sheets on classroom demonstrations and experiments.

● (Order the following from the Superintendent of Documents, U.S. Government Printing Office, Washington 25, D. C.);

Analytical Standards for Trace Elements in Petroleum Products, by H. S. Isbell, R. Stuart Tipson, J. L. Hague, B. F. Scribner, W. Harold Smith, Clarence W. R. Wade and Alex Cohen, National Bureau of Standards Monograph 54, October 1, 1962, 23 pages, 25 cents.

Bibliography on Atomic Transition Probabilities, by B. M. Glennon and W. L. Wiese. National Bureau of Standards Monograph 50, issued August 1, 1962, 43 pages, 35 cents.

Experimental Transition Probabilities for Spectral Lines of Seventy Elements, derived from the National Bureau of Standards tables of spectral-line intensities, this monograph contains the wavelength, energy levels, transition probability and oscillator strength of 25,000 lines between 2000 and 9000A for 112 spectra of 70 elements. 1962. 562 p. il. Catalog No. C13.44:53. Cloth, $4.25.

● Applied Science Laboratories, Inc., State College, Pa. has just released *Catalogue #5* which lists over 100 high purity fatty acid chemicals, triglycerides, cholesteryl esters, uniformly tagged C^{14} fatty acid chemicals and calibration standards for gas chromatography.

New Chemicals

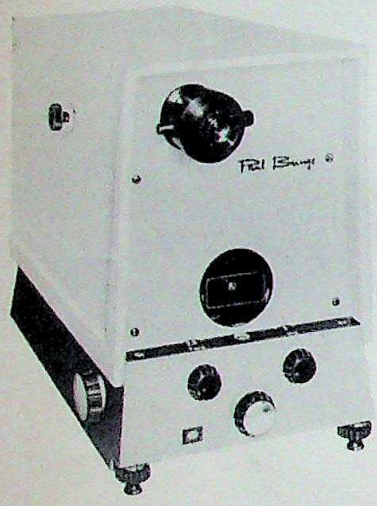
◇ The Ames Laboratories, Inc., 200 Rock Lane, Milford, Connecticut, offers 2-amino-1-propanol hydrochloride (dl) as well as a sheet describing several new amines now available.

◇ Specifications and prices of a transparent, completely colorless Penn Drake C773 oil, for constant temperature baths is available from Research Dept., Pennsylvania Refining Co., Cleveland 4, Ohio.

Miscellany

★ A woman's post-graduate fellowship in chemistry, mathematics or physics has been awarded to Radcliffe College by the DuPont Company. The grant was made to call the attention of scientifically talented women to the growing opportunities for them in industry, education and government and to encourage them to undertake advance studies in science. The fellowship will go to a promising student specializing in one of the three disciplines who is completing her first year of graduate study at Radcliffe. She will be selected by the college. The total grant of $10,000 will cover tuition plus a monthly stipend of $200 for two further years of full-time study, or the equivalent, leading to the Ph.D. degree, and a grant to the college.

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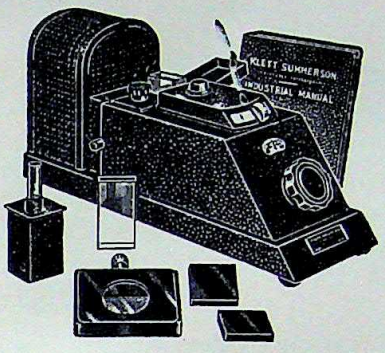
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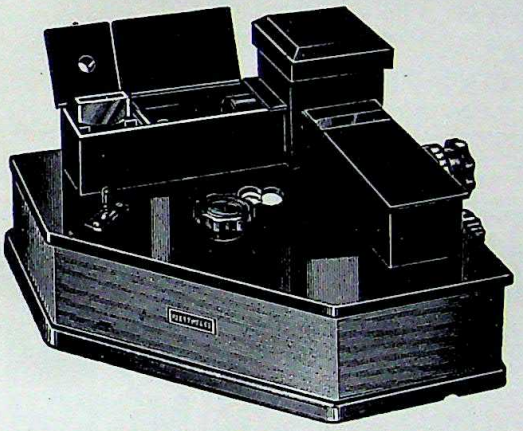
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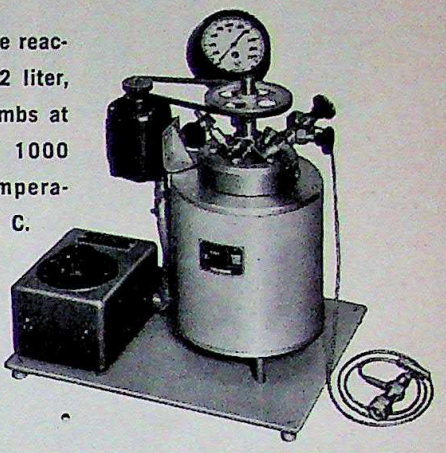
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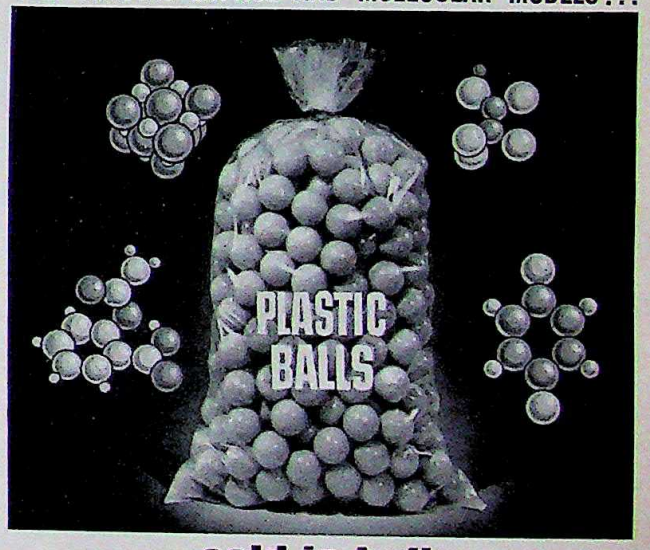
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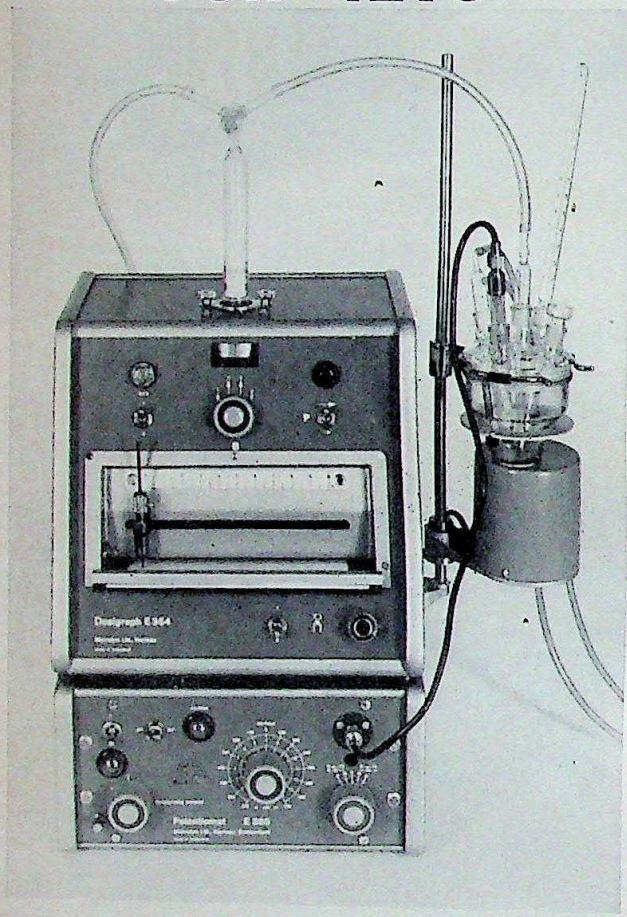
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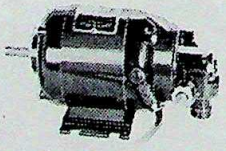
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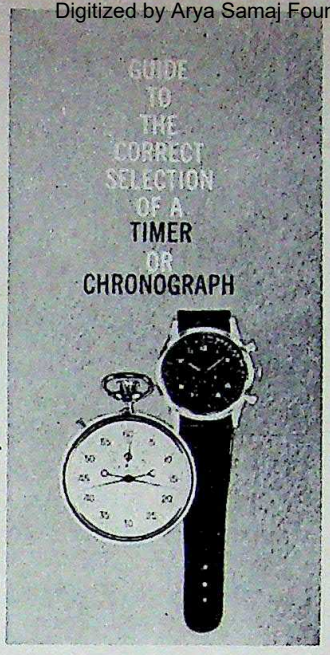
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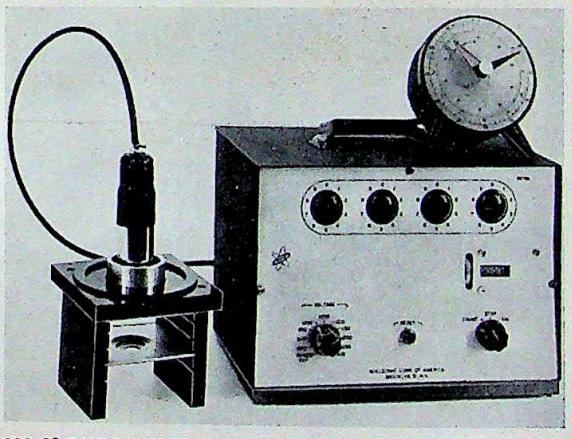
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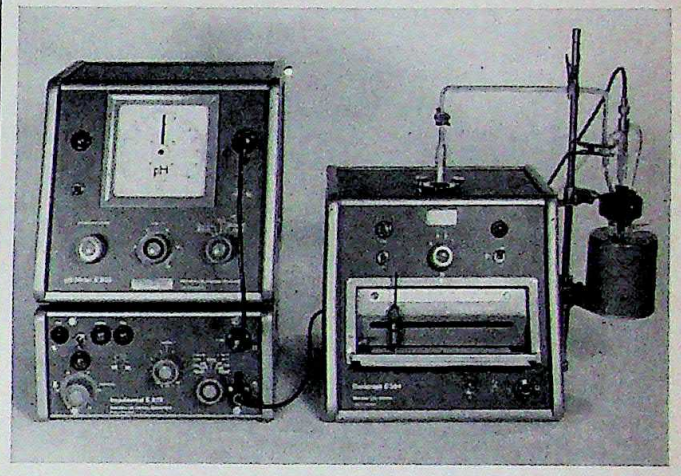
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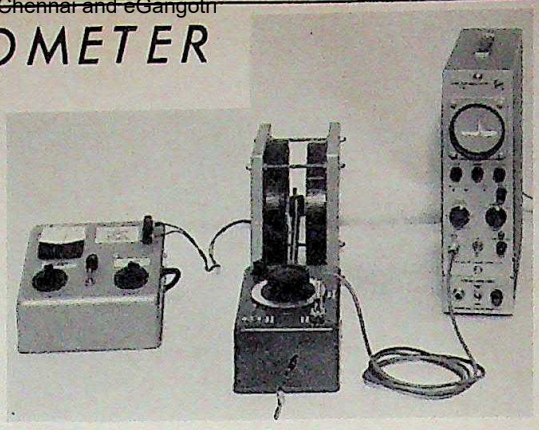
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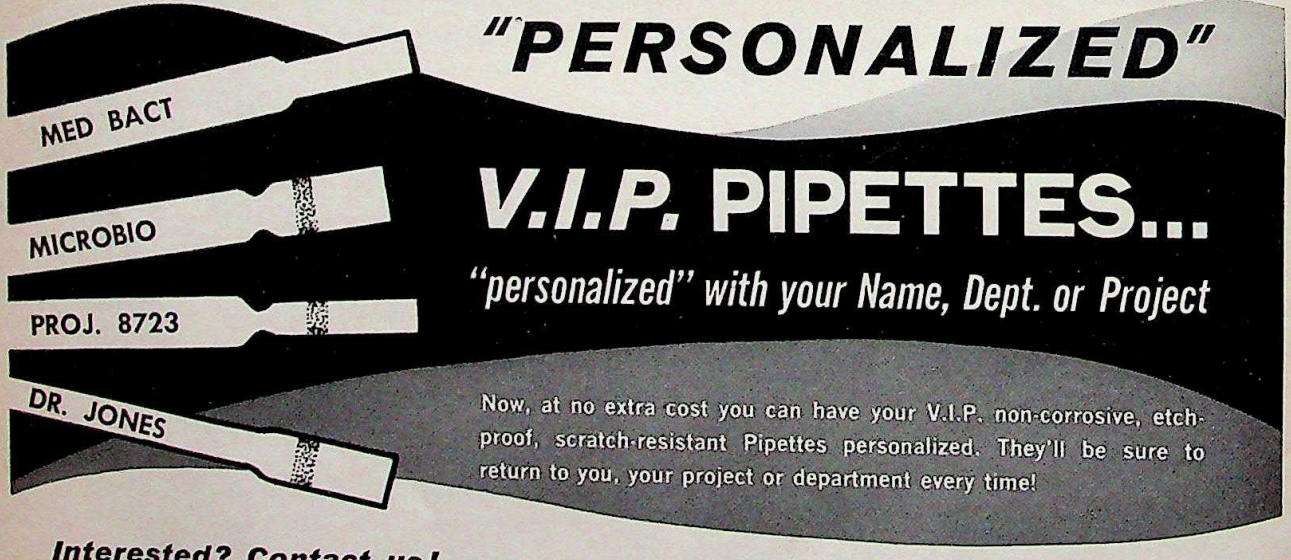
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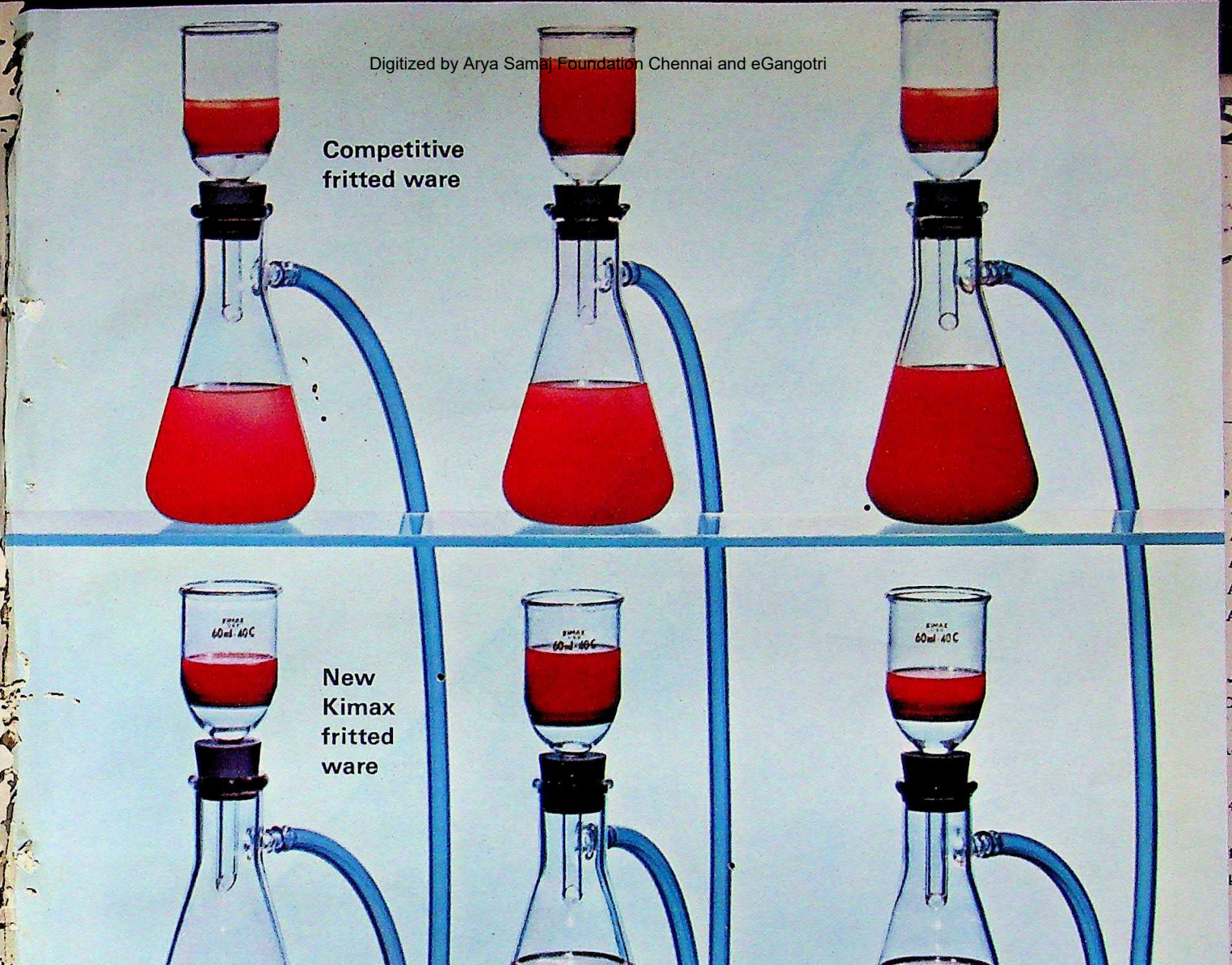
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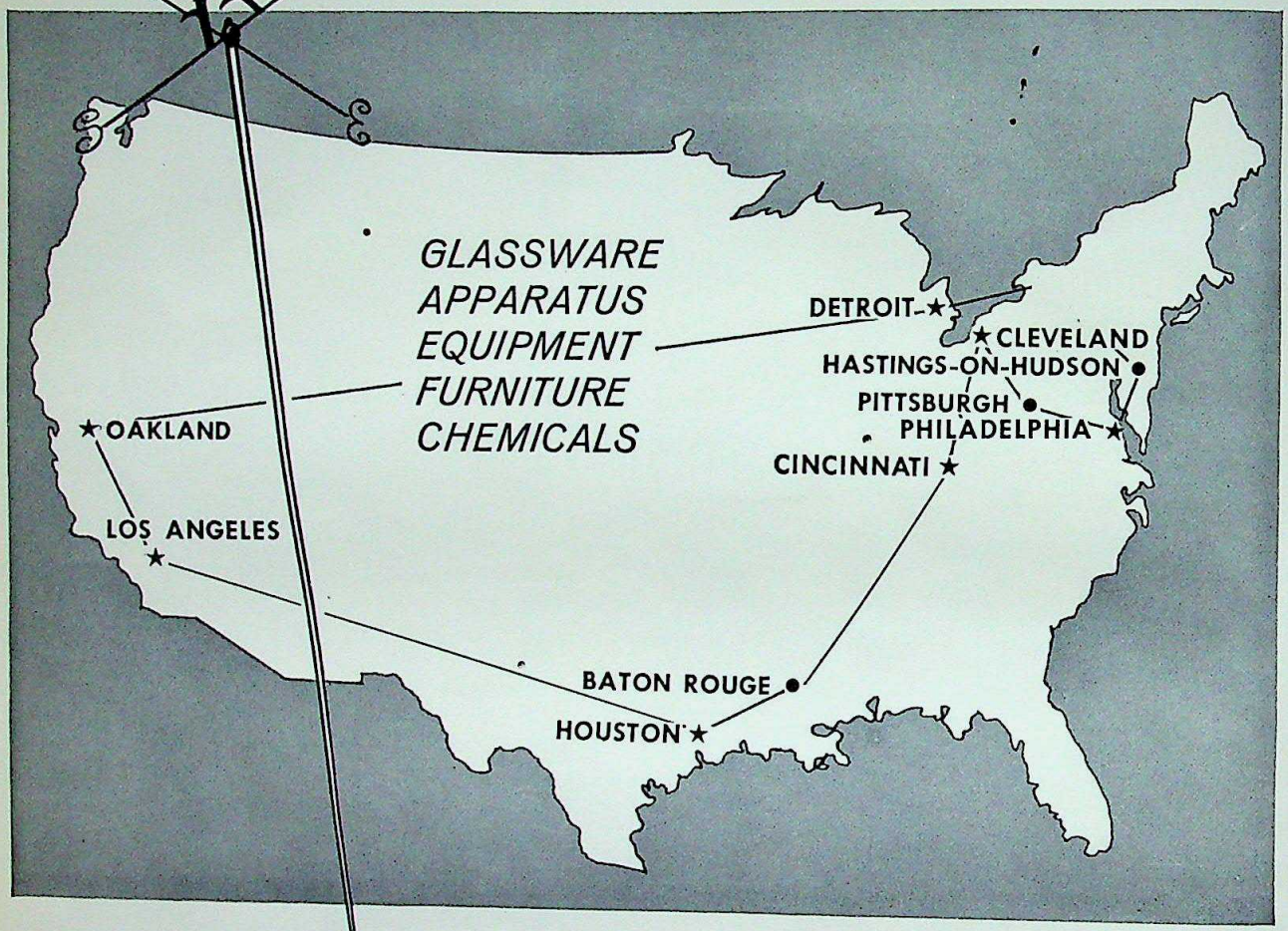
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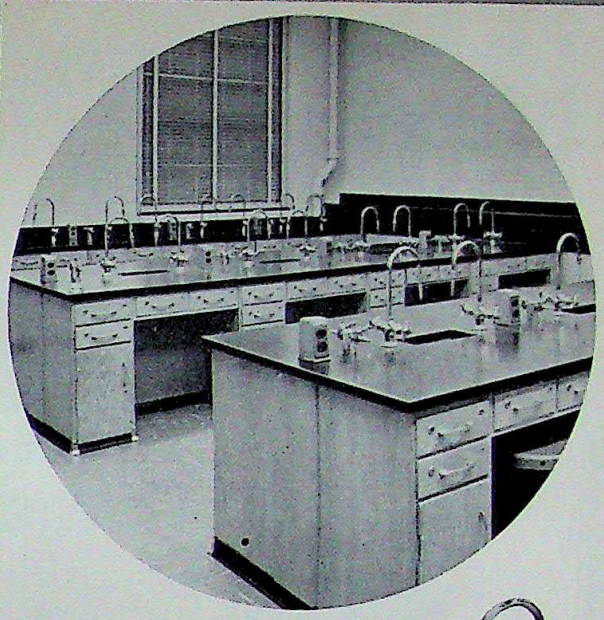
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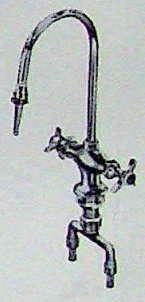
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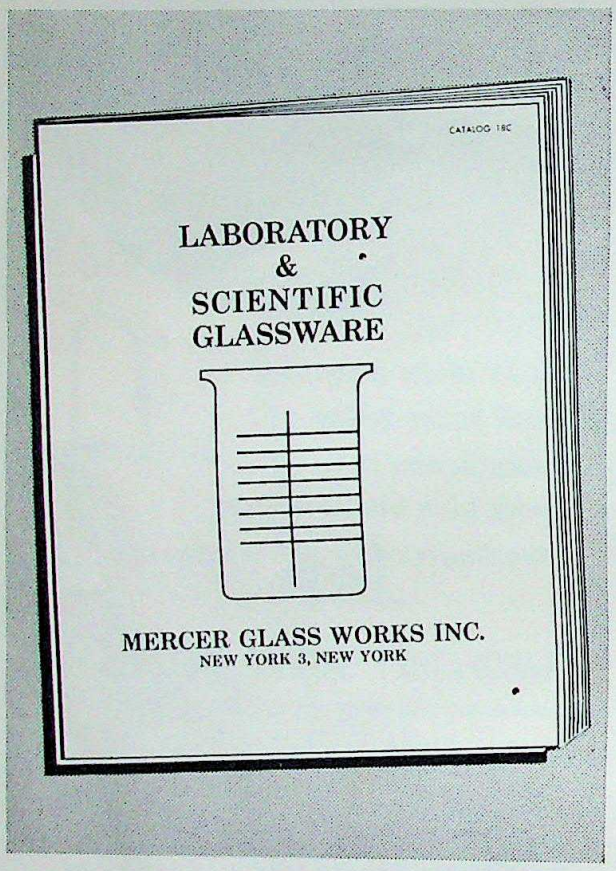
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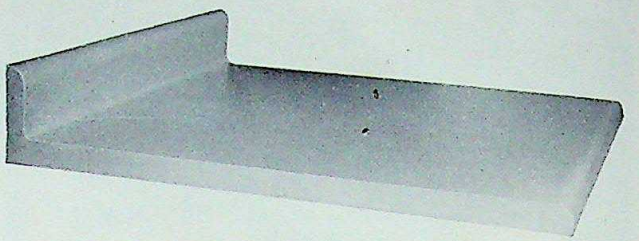
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Princeton University

3. HYDROGEN *(continued)*

B. Preparation of Hydrogen

4. FROM ELEMENTS PLUS SODIUM HYDROXIDE

Dem. 74—Silicon + NaOH

To show: Preparation of hydrogen from Si + NaOH.

Materials: Cell C-g2(SD-7), silicon, NaOH-aq.

Procedure: Place a few grains of silicon in a culture tube and project. Now fill the tube one-half full of sodium hydroxide. Test with a match.

Observations: Vigorous reaction.

Reference: ADAMS, C. S., *J. Chem. Educ.*, **7**, 349 (1930).

Dem. 75—Aluminum + NaOH or HCl

To show: Preparation of hydrogen from aluminum with NaOH or HCl.

Materials: Cell C-g2(SD-7), aluminum turnings or granular aluminum, NaOH-aq., HCl-aq.

Procedure: Place a $^1/_4$-in. layer of Al turnings in two culture tubes. Project. To each add half a tubeful of NaOH-aq. and HCl-aq. respectively.

Observation: There is an induction period before reaction sets in, probably while the Al_2O_3 is being cleaned off the surface. With our samples the NaOH began to react immediately, the HCl only after 5 min.

Reference: WEAVER, E. C., *J. Chem. Educ.*, **24**, 48 (1947).

5. FROM LITHIUM HYDRIDE

Dem. 76.—Lithium Hydride + Water

To show: A convenient method for preparing hydrogen by the action of water on lithium hydride. $LiH + H_2O \rightarrow LiOH + H_2$.

Materials: Lithium hydride pills (Hydripills), 400 ml. beaker, plastic jar $4^1/_2$ inches high × 2 inches in diameter.

Procedure: Fill the jar to the brim with water. Over it place the dry beaker. Quickly invert; the water still stays in the jar. Now slip a $^{10}/_{32}$-inch Hydripill into the beaker. Lift the jar slightly and as gas begins to be generated, let it fill the plastic jar. Cease collecting while there is still a quarter-inch of water in the jar, screw on the plastic cap. This water seal will keep the hydrogen in the jar indefinitely.

Observations: Hydrogen is very gently generated. One $^{10}/_{32}$-inch Hydripill, about the size of an aspirin pill, will generate 570 ml. of hydrogen.

Notes: 1. Hydripills can of course also be used in any of a number of other generators, such as device G-1, or in culture tubes in G-g2 (SD-7).

2. Hydripills are sold by Metal Hydrides Incorporated, Congress Street, Beverly, Mass. I am indebted to Dr. Donald H. Powers who called my attention to Hydripills and furnished samples.

C. Physical Properties of Hydrogen

Dem. 77—Diffusion Bottle

See Special Devices SD-12. Lowering an inverted beaker of hydrogen over a porous cup causes a fountain to squirt from the bottle into the classroom.

Dem. 78—Diffusion Cell

See Special Devices, SD13-14. Lowering an inverted beaker of hydrogen over a porous cup causes (*a*) a bell to ring and (*b*) a fountain to squirt into a cell.

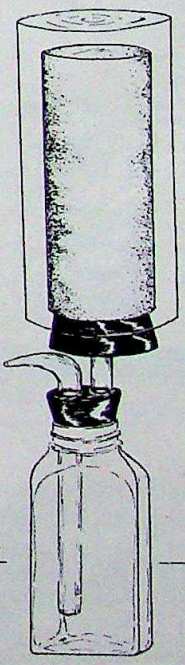
SUPPLEMENTARY DEVICES

SD-12—Diffusion Bottle

This device was developed by Kenneth Jackman of The Hill School, Pottstown, Penna.

Construction of SD-12: The figure is self-explanatory. The dimensions are not critical, but the exit tube should be short. The water can be tinted with red food coloring.

Use: (*a*) Invert a beaker of hydrogen over the porous cup: a fountain squirts out into the classroom. (*b*) Remove the beaker: action is reversed and the liquid descends into the exit tube.



SD-12

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SD-13—Diffusion Cell—Bell

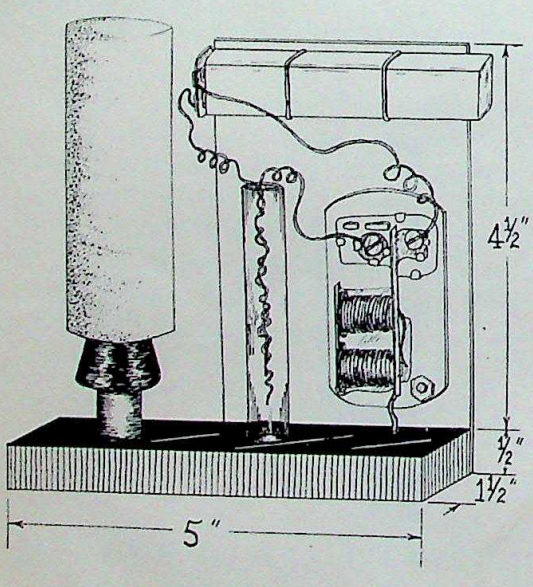
To show: Graham's Law of Diffusion: rate of diffusion H_2: air = $\sqrt{\text{densities air:H}_2}$.

Materials: Small buzzer or bell, small $1^1/_2$ volt battery, insulated No. 28 stiff wire, $5 \times 1^1/_2 \times {}^1/_2$ inch black plastic, $5 \times 3 \times {}^1/_8$ inch clear plastic, $3 \times {}^5/_8$-inch clear plastic, $3 \times {}^3/_8$-inch clear plastic, machine screw, and nut, No. 5 rubber stopper, No. 700 Coors porcelain porous cup 30mm x 76mm; mercury.

Construction of Device SD-13. See Figure SD-13, which is self-explanatory. Holes are bored in the plastic base to form the gas-passage from one vertical tube to the other. Then the exit of the horizontal hole is plugged and sealed with a Plexiglas rod. The Plexiglas tubes are cemented into holes bored in the base. Wires from the battery and electric bell should be fine but stiff, so that they can be twisted together inside the outside two holes bored in the smaller vertical tube. The bare tip of one wire commences below the insulation of the other wire.

Procedure: Prepare hydrogen from Hydripills (Dem. 76), sodium-lead alloy (Dem. 68), or zinc plus acid. Fill a plastic jar $4^1/_2$ inches high $\times$ 2 inches in diameter with the hydrogen. Set Device SD-13 on the stage and project. (a) Now bring the inverted jar over the porous cup. (b) Remove the jar.

Observations: (a) The hydrogen diffuses into the porous cup faster than the air in the cup can diffuse out. This builds up pressure in the cup, forcing the mercury up into the smaller tube where the electrical circuit is completed. The bell rings. (b) When the plastic jar is removed from the porous cup the action reverses; the hydrogen diffuses out faster, creating a partial vacuum, and the mercury in the smaller tube falls, breaking the circuit.



SD-13

SD-14—Diffusion Cell—Water Spiral

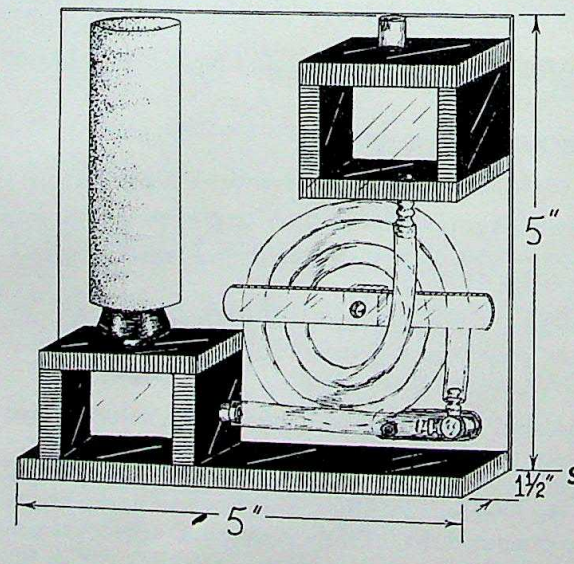
To show: Graham's Law of diffusion: rate of diffusion H_2: air = $\sqrt{\text{densities air:H}_2}$.

Materials: Black Plexiglas: one piece $5 \times 1^5/_8 \times {}^1/_4$ inches, four pieces $1^1/_4 \times 1^1/_2 \times {}^1/_4$ inches, two pieces $1^3/_4 \times 1^1/_2 \times {}^1/_4$ inches, three pieces of small Plexiglas tubing to fit a foot of clear plastic tubing. Clear Plexiglas: one piece $5 \times 5 \times {}^1/_8$ inches, two pieces $2^1/_4 \times 1^1/_4 \times {}^1/_8$ inches, one piece $1^1/_4 \times 1^5/_8 \times {}^1/_{16}$ inches, one piece $3 \times {}^1/_4 \times {}^1/_8$ inches, one piece ${}^1/_4 \times {}^1/_4 \times {}^1/_4$ inches. No 5 rubber stopper, No. 700 Coors porcelain porous cup 30 mm $\times$ 76 mm, red food coloring.

Construction of Device SD-14. See Figure SD-14. Cement the tubes in place before attaching the boxes to the back plate. The two boxes should be identical in size and shape to convey the idea, during projection, that as one box empties of liquid the other fills. The pet-shop valve is useful in slowing the movement of the liquid in the plastic tube to a relatively slow rate; also the valve can be closed with the liquid in the lower box for storage.

Procedure: Prepare a plastic jarful of hydrogen from Hydripills (Dem. 76) or sodium-lead alloy (Dem. 68), or zinc plus acid. Set device SD-14 on the stage and project. (a) Now bring the inverted jar of hydrogen over the porous cup. (b) Remove the jar.

Observations: The hydrogen diffuses into the cup so much more rapidly than the air diffuses out that pressure is built up in the plastic box, forcing the colored liquid to spiral through the tubing into the upper box. (b) Upon removing the jar, the process reverses, and the rapid escape of hydrogen from the porous cup produces a partial vacuum in the lower box; the red liquid spirals back into the lower box.



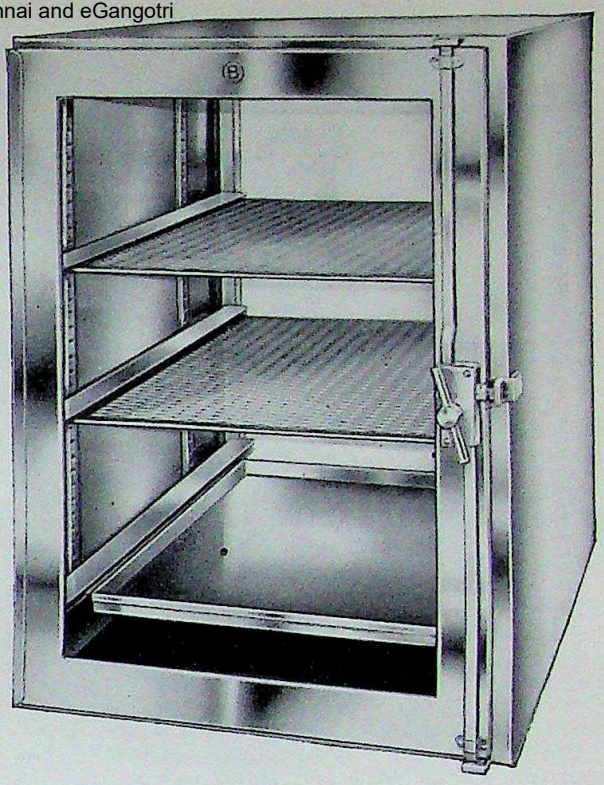
SD-14

(*To be continued in June*)

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a ChemEd feature

CHEMICAL PROJECTS

Research Ideas for Young Chemists

Compiled by **JAY A. YOUNG,** King's College, Wilkes-Barre, Penna.
JOHN K. TAYLOR, National Bureau of Standards, Washington, D. C.

An Easily Prepared Wide Range Buffer Series

See CARMODY, W. R., *J. Chem. Educ.*, 38, 559-60 (1961).

A series of buffer solutions, varying by 0.5 *p*H unit, from a *p*H of 2.0 to 12.0 can be prepared by following the directions given in this article. Only three common reagents, in two stock solutions, are required.

Questions:

Professor Carmody indicates that this series of buffer solutions would be useful in several different kinds of demonstrations and experiments, though he does not mention any specific examples. Can you identify one or more demonstrations or experiments for which this series of buffer solutions would be useful?

The buffer capacity of the series of buffer solutions was measured against hydrochloric acid. Determine the buffer capacity of the series of solutions against other acids and against various basic solutions. Are the results consistent with what you expect? If not, can you account for the results you do obtain?

By including a fourth solute, a weak acid with a *p*K of about 10.5, can you prepare a similar series of buffer solutions with higher buffer capacity in the *p*H range from about 9.5 to 11.5?

Would it be possible to prepare a series of buffer solutions, similar to those described in the article, using weak bases instead of weak acids?

Can you design a procedure for the preparation of a series of buffer solutions for a narrow range, say from *p*H 3.00 to 4.00 (or any other range), varying in steps of 0.01 *p*H unit?

Heat of Precipitation

See CLEVER, H. L., *J. Chem. Educ.*, 38, 470-1 (1961).

Heats of precipitation of insoluble salts can be readily determined using a simple calorimeter constructed from a small beaker, an Erlenmeyer flask, some insulation, a rubber stopper, and a thermometer calibrated in 0.1°C intervals. The results are precise to within ±5% when care is exercised.

Questions:

Using the procedure outlined in the article, and the same assumptions concerning the densities and specific heat capacities of the solutions, determine the heats of precipitation of several slightly soluble substances. Is there any relation between the results you have obtained and the electronegativities of the ionic species involved? Or, is there some other similar relationship which you can elicit from a tabulation of your results? Account for the relationship you have discovered and test your explanation by further laboratory work.

Can you perform the experiments indicated above, but using a better calorimeter than the one described in the article? In such work, is it still reasonable to make the same assumptions concerning the densities and specific heats of the solutions, or should these be more precisely evaluated?

Heats of solution are identical, except for algebraic sign, with heats of precipitation. A procedure for the determination of the heat of solution of sulfuric acid is described by E. WOLTHUIS, ET AL., J. CHEM. EDUC., 38, 472-3 (1961). With suitable modifications, this procedure can be used to determine the heats of solution of other solutes. Select a moderately soluble salt and determine both its heat of precipitation and its heat of solution by direct experimental measurements. Are your results comparable, except for algebraic sign? If not, what modifications must be made in your procedure so that the results do agree?

A Simple Demonstration of Some Precipitation and Solubility Effects

See MATIJEVIC, E., *et al.*, *J. Chem. Educ.*, 38, 397-9 (1961).

This article could be subtitled, "When Solubility Product is Not Constant." It is a thorough, and clear, discussion of the phenomena which are observed when excessive amounts of silver nitrate are added to solutions of sodium (or potassium) bromide and when excessive amounts of alkali bromide are added to solutions of silver nitrate. Due to the formation of complex ions, clear solutions, turbid suspensions of silver bromide, and almost clear sols, are formed under certain conditions. These observed facts can be classified and clarified by a graphical tabulation which the authors call a solubility diagram.

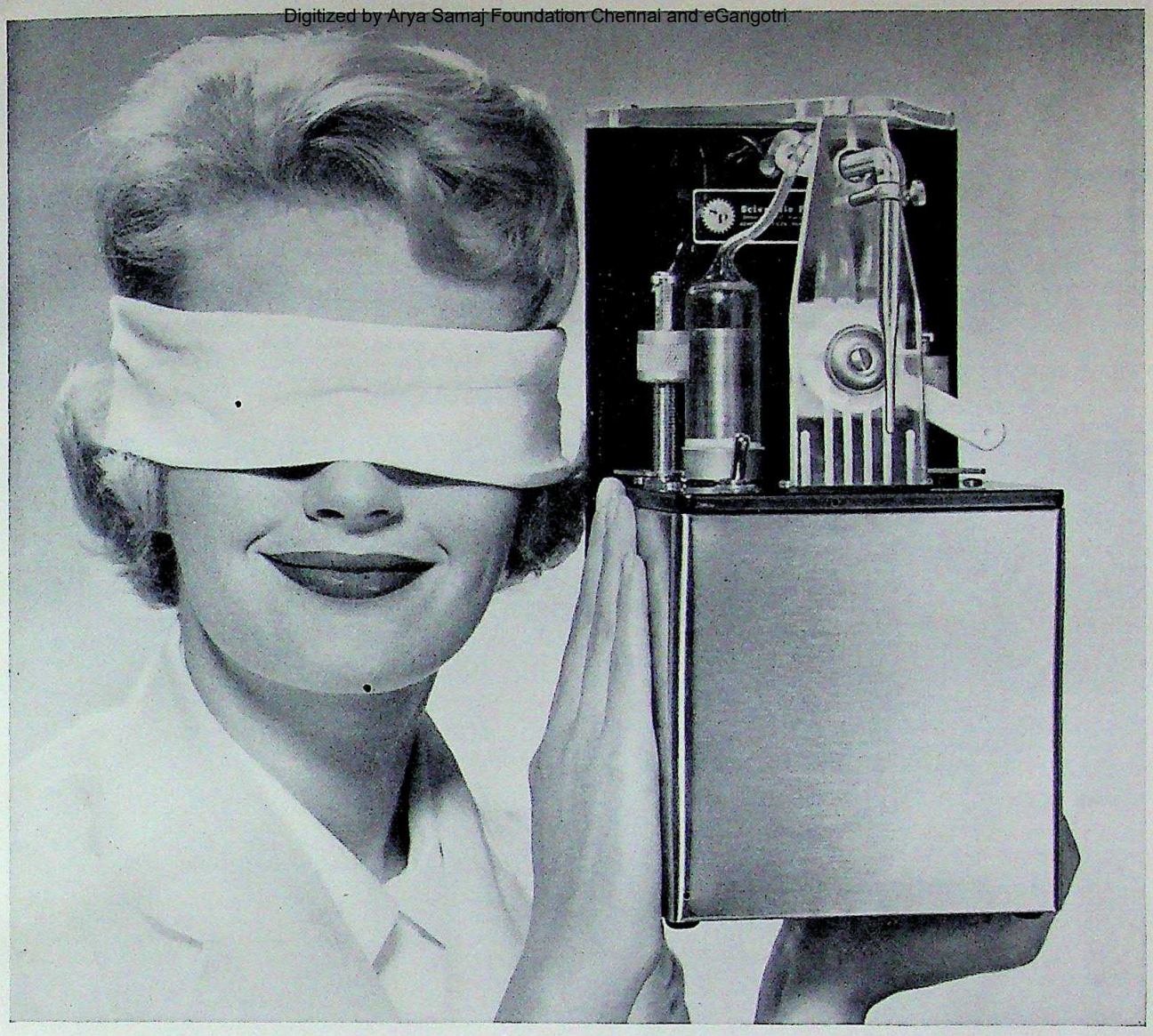
It would be interesting and instructive to construct solubility diagrams for other so-called insoluble salts instead of silver bromide. Such an investigation is strongly recommended to the interested student.

Question:

Select any other insoluble salt which can be formed by mixing two solutions and from the data you obtain when varying the amounts and concentrations of the reagents, construct a diagram similar to the upper portion of the figure in the article. If the necessary optical apparatus is available, also construct several diagrams similar to the lower portion of Figure 1, or construct a three dimensional representation of your results. Identify each different area in your diagrams, and account for the formation of precipitate, either as a turbid suspension or almost clear sol, and account for the presence of true solutions by further laboratory studies of the systems which exhibit these phenomena.

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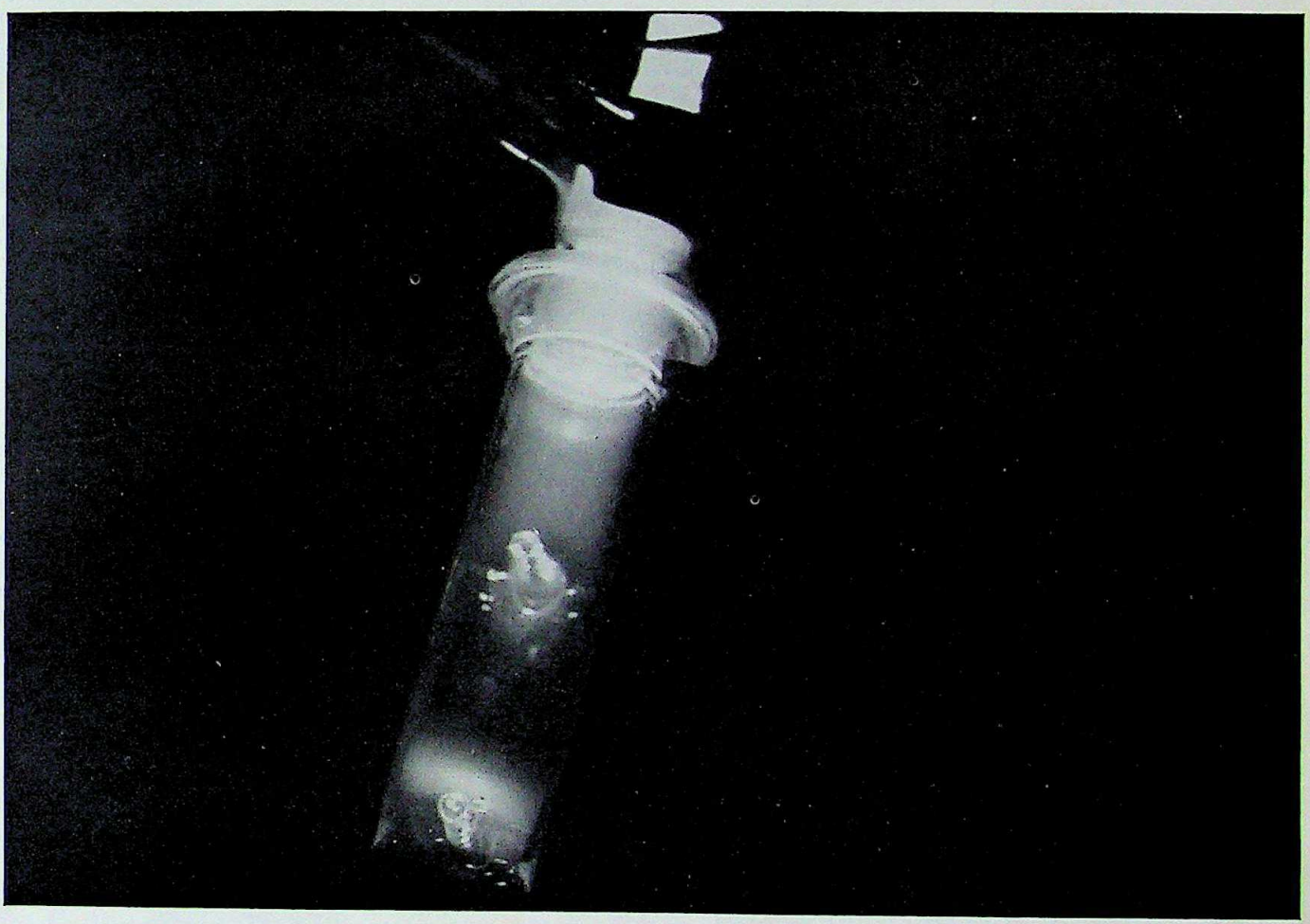
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Oxygen atom reactions with saturated hydrocarbons yield products which suggest a new concept in diradical chemistry.

In studies of ground-state oxygen atom reactions, Dr. Franklin J. Wright, Esso Research scientist, reacted nitric oxide with nitrogen that had been partially dissociated into atoms by microwave discharge. Oxygen atoms were generated in the absence of molecular oxygen, thus avoiding side reactions. Using equipment shown above, carbonyls and aldehydes such as acetone and iso-butyraldehyde were the principal derivatives from the reaction with isobutane. At the same temperature (30° C.), oxidation with molecular oxygen yielded alcohols and hydroperoxides.

Considerable evidence indicates that hydrogen abstraction by diradical oxygen atoms plays only a minor role. The reaction products apparently are formed more directly by replacement of two groups on the reacting hydrocarbon with an oxygen atom. Whether this occurs simultaneously, or step-wise, has yet to be established.

This study, revealing the unusual and unexpected reactivity of diradical oxygen atoms, suggests that other diradicals now being investigated may also display equally interesting chemistry. Research such as this is helping to give a deeper understanding of a new and promising field.

...adapted from the scientist's notes
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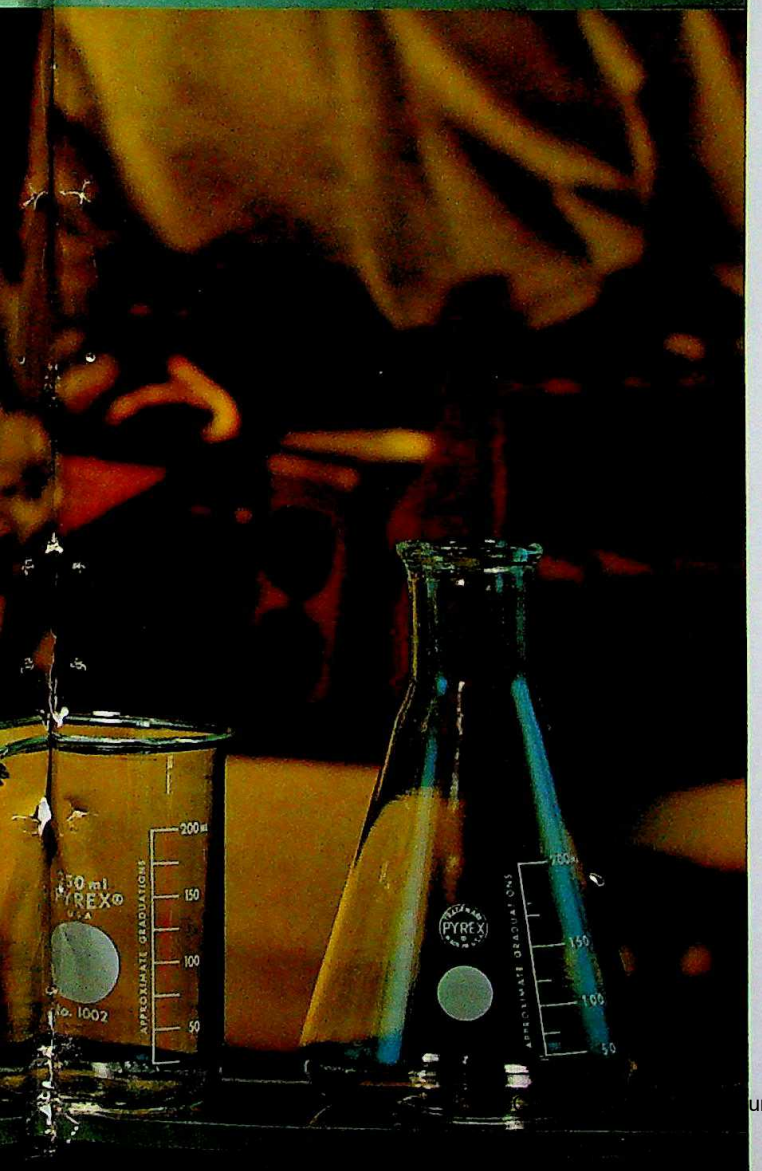
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Martin D. Kamen
University of California
San Diego

The Early History of Carbon-14

When, how, and why was carbon-14 discovered?

As T. S. Kuhn has remarked (*1*), discovery is seldom a single event that can be attributed wholly to a particular individual, time, or place. He notes that some discoveries, such as those of the neutrino, radio waves and missing isotopes or elements, are predictable and present few problems, as far as establishment of priority is concerned. Others, such as the discoveries of oxygen, X-rays, and the electron, are unpredictable. These put the historian in a "bind" when he tries to decide when, how, who, and where of the discovery. Much more rarely does he have a basis for an answer to the question "why?"

I propose in this narrative of the "prenatal" history of ^{14}C, to provide the answers to my leading questions. These will make a story which is a fragment of the whole record that must be constructed by future historians who seek to probe the events of a period in which there has been an unparalleled impact of intellectual curiosity and scientific creativity on the structure of society.

The tremendous outburst of technology in the past half-century, consequent to the rise of nuclear science, has crowned man's quest for the philosopher's stone so successfully as to be hardly credible even to the most optimistic alchemist. Tracer methodology, an offspring of nuclear science, has provided essential support for the ever-widening and deepening knowledge of structure and function in biological systems, expressed as the dynamic science of molecular biology.

These developments have profound, but unknown, implications for the future of our social structures. They obviously bring with them an unexampled load of grist for the mills of cultural historians, social scientists, and philosophers. Perhaps the novelists will dig into the record of these exciting times for fresh insights into the age-old drives of mankind.

Carbon-14, the long-lived carbon isotope, is the most important single tool made available by tracer methodology, because carbon occupies the central position in the chemistry of biological systems. Thus, it plays, and will continue to play, an essential role in the elucidation of biochemical mechanisms—knowledge of which is essential in the further development of molecular biology. Obviously, the circumstances surrounding its discovery are valid objects of interest for the historian.

I am happy that this opportunity has arisen to record a deeply felt personal tribute to two former associates, Dr. Franz N. D. Kurie and Dr. Samuel Ruben. The interruption of Dr. Kurie's career by a debilitating illness a few years ago deprived nuclear physics of a foremost investigator. The untimely death of Dr. Ruben, at the age of 29 while engaged in research in chemical warfare in 1943, was an unmitigated catastrophe for modern biochemistry.

The Initial Phases, 1934–6

In the early 1930's, nuclear physicists, well-immersed in the great traditions of the Cambridge school led by Ernest Rutherford, were concerned primarily with observations of processes associated with the scattering of elementary nuclear particles by various atomic nuclei. Reports in those times show painstaking determinations of range-energy relations for the fundamental projectiles (protons, deuterons, alpha particles). The energies used did not exceed ~10 Mev, because of the limitations set by the relatively primitive accelerators and by the radiation characteristics of available naturally radioactive materials. The rationale for such work, which often involved much labor and tedious attention to detail, was that if enough precise facts were put together, accurate binding energies for nuclei could be deduced. From these, it was reasoned, could be derived a solid basis for further attack on the problem of the nature of nuclear forces.

By 1933, such data—as binding energies, angular distributions in scattering experiments, etc.—had demonstrated that nuclear forces could be described as analogous to saturation exchange forces, like those

The Cover



The photograph shows the author installing a B_2O_3 target for cyclotron bombardment. This and the other photographs accompanying the text were taken by *Life* photographer Peter Stackpole in 1938 and are used here by special permission of *Life Magazine*. The editor also acknowledges with thanks the gracious cooperation of Dr. Philip Abelson, Editor of *Science*, and one-time associate of Dr. Kamen. The text of this paper will also appear in the May 10 issue of *Science*.

This paper is an abridged version of a lecture presented at the meeting of the American Chemical Society in Los Angeles, California, April, 1963, on the occasion of the 1963 Award for Nuclear Applications in Chemistry.

[1] A brief account, concerned mainly with technical aspects, has appeared previously, see KAMEN, M.D., "Isotopic Tracers in Biology," 3rd ed., Academic Press, New York, 1957, p. 300 *et seq.*

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postulated previously for chemical bonding. The so-called "alpha-particle" model of the nucleus already contained the seeds of what was to be the full-fledged modern "shell" theory of nuclei, to be developed later by Maria Mayer, Eugene Feenberg, and others.

As to my part in this, I was a young eager student and had just begun doctoral research, using the Wilson cloud chamber to study the angular distribution of neutrons scattered in collisions with protons and other nuclei. These researches were part of a general program initiated in the laboratory of Professor W. D. Harkins in the Chemistry Department at the University of Chicago (*2*). My decision to work in this field was largely owing to the influence of Dr. D. M. Gans, Professor Harkins' associate and also an assistant professor in the department. I am happy to record here my great debt to Dr. Gans and also to Dr. Henry W. Newson, my immediate predecessor in the research. Both of these scientists were most patient and helpful in my successful induction into a research career.

Most significantly for this history, similar work was also underway at Yale, where Dr. F. N. D. Kurie was investigating neutron-induced disintegration of light elements, and had obtained certain anomalous results for the angular distributions of protons in collisions with neutrons. In 1934 he proposed a radical interpretation (*3*) of certain events he noted in the cloud chamber. When nitrogen was exposed to fast neutrons, for instance, he found that in some cases the ejected nucleus exhibited a very long, thin track. This he ascribed to a proton, rather than an alpha particle. Thus, he supposed that the usual reaction, ^{14}N (n, $^{4}He)^{11}B$, was accompanied by a less frequent but readily observable reaction, $^{14}N(n, ^{1}H)^{14}C$. (As far as I am aware, this is the first suggestion in the literature that ^{14}C might exist.) Kurie also suggested, however, that the tracks he was observing might be those arising from ^{2}H, or even ^{3}H, so that the reactions, $^{14}N(n, ^{2}H)^{13}C$ and $^{14}N(n, ^{3}H)^{12}C$, were also possible. In fact, he felt the reactions with emission of ^{2}H and ^{3}H were more likely because they resulted in nuclei of known stability.

What was radical about Kurie's suggestion was the idea that something other than an alpha particle could emerge in a disintegration of a nucleus like ^{14}N. Thus the physicists at the time assumed from their everyday experience that the alpha particle was much the most likely nucleon to be formed in such a nuclear reaction. This belief found a ready basis in the relatively great stability of the alpha-particle which was considered to exist as an entity in all nuclei because of its relatively enormous binding energy per nucleon, and because invariably in natural radioactivity it was the only heavy nucleon ejected.

In the meantime, T. W. Bonner and W. M. Brubaker (*4*) published observations on the energies of recoils induced by neutrons in inelastic collisions with nitrogen nuclei. Assuming the usual reaction, $^{14}N(n,^{4}He)^{11}B$, they calculated from the mass values given by Hans Bethe (*5*) that Q, the heat of reaction, was ~1.5 Mev. Most significantly, however, Bonner and Brubaker (*3*, *4*) and W. Chadwick and M. Goldhaber (*6*, *7*), independently, reported that the disintegration of ^{14}N occurred also with *slow* neutrons.

This, it turned out, was the crucial observation in the "prenatal" history of ^{14}C, because it prompted a re-evaluation of the assumptions on which analyses of the nitrogen disintegration tracks were based.

Chadwick and Goldhaber had detected disintegrations in an ionization chamber connected to a linear amplifier and oscillograph. From the size of the oscillograph deflections they had deduced that Q was ~0.5 Mev. Bonner and Brubaker had used a cloud chamber and observed a group of tracks with a sharply defined range of 1.06 cm air (STP) which they thought to be alpha particles. On this basis, they had calculated a Q value of 2.33 Mev. The discrepancy in the two Q values was far beyond any experimental error. W. E. Burcham and Goldhaber (*8*) then were inspired to suggest that both sets of data were referred to the wrong reaction, and that if the disintegration were assumed to take place with proton emission, i.e., $^{14}N(n,^{1}H)^{14}C$, then the value of Q taken from the range observed by Bonner and Brubaker, became 0.58 Mev, in good agreement with the value of Q deduced from the ionization measurements. Bonner and Brubaker not only concurred, but advanced further evidence in support of this suggestion by noting that when they measured Q for a related reaction, $^{11}B(^{2}H,n)^{12}C$ they found a value of 13.5 Mev, which, together with Q values known for some other reactions, enabled them to construct a reaction cycle in which the $^{14}N(n,^{4}He)^{11}B$ reaction turned out to be endergonic, $Q = -0.28$ Mev, rather than exergonic, $Q = 2.33$ Mev. Thus, the alpha particle emission could not have taken place with slow neutrons, at least if one believed the rather marginal negative value for Q.

Burcham and Goldhaber proceeded to use the visualization technique of nuclear emulsions, in which they could distinguish more certainly between protons and alpha particles. They showed conclusively (*8*) that alpha particles were not emitted in the slow neutron disintegration of ^{14}N, and proposed that the recoil particles be assigned definitely to the reaction with ^{14}C as a product. They could not exclude experimentally the possibility that ^{2}H or ^{3}H particles, rather than protons, might account for the recoil tracks observed. On the other hand, they remarked that reactions that could produce such particles were unlikely on energetic grounds. Thus, Kurie's original intuitive suggestion based on the appearance of certain unusually thin, long tracks in his cloud chamber experiments of 1933–4, were raised to the status of a practical certainty by 1936.

I think it is safe to say that in the *physical* sense the discovery of ^{14}C had been established by the observations of Burcham and Goldhaber. But as to the discovery of ^{14}C in the *chemical* sense—which I must say has turned out to be the more important—many obstacles lay in the way. Referring again to the remarks of Kuhn (*1*), the discovery of ^{14}C in a physical sense belongs in the "expected" category but its discovery in the chemical sense does not.

The Intermediate Phases, 1936–8

Meanwhile, back at the ranch—so to say—I was plugging away collecting proton recoils produced by collisions with neutrons from a pathetically weak MsTh-Be source of a few millicuries equivalent. By

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the end of 1936, I received a PhD on the basis of results obtained from an analysis of 730 tracks which showed a marked asymmetry in the angular distribution of protons in the energy range from ~0.1 to 3 Mev (*9*). This result confirmed those obtained by Kurie a few years previously (*10*). But, at the time, these results were in contradiction to theoretical expectations. Before this anomaly could be taken seriously, it was required that greater numbers of events be analyzed—an objective quite unrealizable with the feeble neutron sources available. It had taken three years of constant labor to produce and analyze a few hundred proton recoils—in fact, 10 man-hours per track had been required! This statistic shows how slender were the means available for researches in nuclear physics in 1936, which after all is not so long ago.

It was natural in the mid-1930's to look toward Berkeley where Ernest O. Lawrence was assembling the nucleus of a group of young physicists drawn by the prospect of a greatly enhanced particle source—the cyclotron.

Thus, in January of 1937, I found myself at the Berkeley Radiation Laboratory, along with Kurie who had arrived there a short time before. Because of our mutual interest in neutron scattering, we quickly began a collaboration in which we proposed to investigate not only the various apparent anomalies in the neutron-proton interactions, but neutron-nuclear interactions in general. The neutron fluxes available with the cyclotron, even in its primitive form as the 27-in. machine in 1937, were already four or five orders of magnitude greater than any with which we had been familiar.

Unfortunately, this neutron flux was not a well-collimated beam with minimal energy spread. The cyclotron contained innumerable scattering sites from which great numbers of neutrons emerged in a welter of undefined directions and energies. To achieve some measure of order in the neutron beam, a major effort was begun by Lawrence and his group, with responsibility vested largely in Dr. Arthur Snell. The procedure was to lead the deuterium beam away from the main vacuum accelerating chamber so that it would hit a beryllium target at some distance from the scattering bulk of the cyclotron. The emergent neutrons from the $^{9}Be(^{2}H,n)^{10}B$ reaction were to be piped through a hole in the water shield around the cyclotron. It was hoped that, with judicious use of auxiliary absorbers, the whole effect of this effort, called "snouting," would produce a relatively well-collimated intense beam of neutrons with a small energy spread downward from the maximum available in the reaction.

Kurie and I found that a cloud chamber filled with hydrogen as target, placed at either side of the hole, showed relatively few recoil pictures compared to an enormous yield when the chamber was directly in front of the hole. A typical single expansion, in front of the snout hole with an exciting deuteron beam of a few microamperes incident on the beryllium target, exhibited more recoil tracks than either Kurie or I had seen in all our previous experience with naturally radioactive sources of magnitude then available, e.g., hundreds of millicurie equivalents of Po or Ra, mixed with Be.

Mindful of the previous results on ^{14}C production, we decided to exploit them in our researches on neutron disintegration of ^{14}N. The slow neutron reaction on ^{14}N with its characteristic recoil product—protons of a homogeneous range of 1.06 cm in air as dictated by the Q value of 0.58 Mev—manifested itself almost every other expansion in the cloud chamber as a short, stubby track with a knob on the starting end. This track arose from the proton which, because of its relatively low mass, took up practically all the energy of the reaction as kinetic energy, while the knobby stub was the ^{14}C recoil, which because of its relatively high mass, possessed very little of the kinetic energy released in the reaction. These characteristic short, stubby tracks provided a convenient and accurate internal monitor for calibration of the stopping power of the nitrogen gas–water vapor mixture in the cloud chamber. In this way, we solved a very bothersome technical problem—the precise value of stopping power to use in calculations of ranges for determinations of recoil energies. Thus, ^{14}C was sufficiently well established as an entity by early 1937 so that it could be used in the calibrations of cloud chamber experiments!

However, nothing was known about its physical characteristics. One could attempt some predictions. First, it seemed certain that ^{14}C was radioactive and that it must emit negative β-rays in transformation to ^{14}N. This followed from the observation that in all known cases among the elements of low atomic number, there were no examples of neighboring isobaric pairs in which more than one of the pair was stable, e.g., as in the pairs, ^{6}He–^{6}Li, ^{7}Be–^{7}Li, ^{10}Be–^{10}B, ^{11}C–^{11}B, etc. So, one might expect that for the isobaric pair ^{14}C–^{14}N, the stability of ^{14}N required that ^{14}C be unstable and decay to ^{14}N by transformation of a neutron into a proton, with emission of a negative beta particle and a neutrino. Secondly—and here a great uncertainty arose—the rate of decay could be expected to be fairly rapid, because in two known analogous cases in which a nucleus with two excess neutrons decayed to a nucleus with equal numbers of neutrons and protons, i.e., ^{6}He–^{6}Li and ^{10}Be–^{10}B, the expected decay rate was in quite good agreement with those actually observed. Thus, ^{6}He, with an upper energy limit for β-rays of 3.5 Mev and a spin difference no more than 1 unit possible, could be expected to decay with a period of the magnitude 10^{-1} to 10^{1} sec. Its half life was, in fact, 0.8 sec. ^{10}Be with its enormously long half life—of the order of 10^{6}–10^{7} years (*11*)—corresponded to a highly forbidden transition despite a fairly high beta ray energy maximum of ~0.5 Mev. In this case, a high degree of forbiddenness could be rationalized on the basis of the shell model available, i.e., a large spin difference was possible. The case of ^{14}C was quite analogous to that of ^{6}He–^{6}Li, with a maximum spin difference of 1. The lower energy limit to be expected depended on the mass difference between ^{14}C and ^{14}N. Thus, for the production reaction with slow neutrons,

$$(n—^{1}H) = (^{14}C - ^{14}N) + Q$$

For the masses as then known and for $Q = +0.58$, the maximum energy expected for the emergent beta particles was ~0.3 Mev. On this basis, a tentative maximal estimate for the ^{14}C half life of a few hours or days

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was made by P. Morrison and J. Cassen (*10*). Thus, it appeared that ^{14}C was probably quite short-lived. If attempts to make it proved negative, it could be assumed that the half life was too short for the isotope to be isolated, rather than that it was too long, i.e., $t^1/_2$ was expected to be in the order of seconds, rather than centuries.

None of these arguments were wholly convincing for it was recognized that the state of beta decay theory was quite unsatisfactory; nevertheless they were sufficiently impressive to discourage determined efforts to isolate ^{14}C at that time. E. M. McMillan had noted that some very long-lived activities were present in old cyclotron targets and bits of metal scraped from various parts of the acceleration chamber. With what now is seen to be extraordinary intuition, he surmised that these activities could represent radioactive species of Be and C. In an abstract (*11*) submitted to a meeting of the Physical Society in 1936, he described two activities residual in an old Be target. The major activity was a very soft component, with a decay rate consistent with a half life of 10 years or longer. This component, he thought, might be assigned tentatively to ^{10}Be. The other activity which was weaker, but harder, and decayed with a half life of a few months, was suggested as owing to a radioactive isotope of carbon, in particular ^{14}C. In later years (*12*) he published a final summary of work done with S. Ruben in the years 1938–40, in which the activity assigned to ^{10}Be was reassigned with some certainty to ^{3}H. The other activity obviously could not have been ^{14}C, because, as we know now, the half life of ^{14}C is ~5700 years. In an effort to produce ^{14}C by the $^{14}N(n,^1H)^{14}C$ reaction, McMillan exposed solid ammonium nitrate to the intense neutron flux of the 37-in. cyclotron for several months in 1938–1939, but this experiment ended when the bottle containing the salt was inadvertently knocked off the magnet coil tank and smashed.

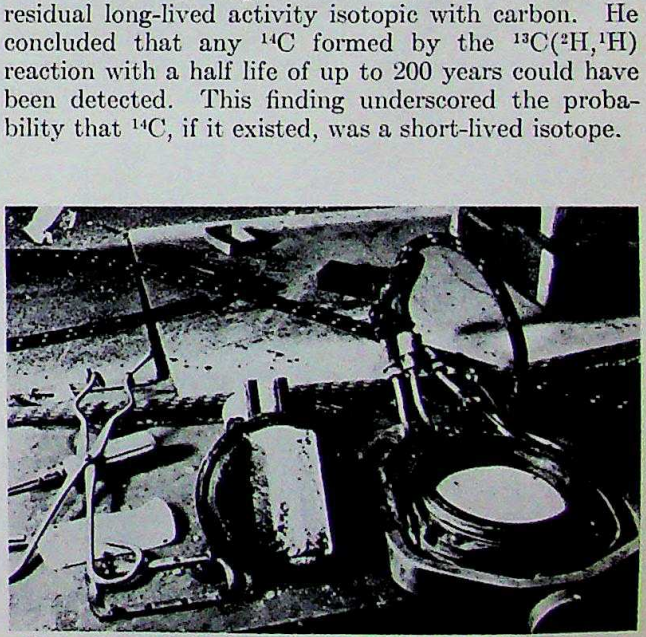
However, a new—and what was to prove decisive—factor entered late in 1937. As we all know, the ancient alchemists' ascribed to the "philosopher's stone" two magical powers—the first was the ability to transmute elements, the second was the ability to banish disease. The old alchemical treatises bear constant witness to the state of mind which supported through centuries what were tedious, disappointing, and often fatally hazardous searches. Even after chemistry was well established and alchemy in some disrepute, Robert Boyle could still make his well-known statement (*13*).

> There may be some agent found out so subtle and powerful, at least in respect of those particular compounded corpuscles, as to be able to resolve them into those more simple ones, whereof they consist.

With the discoveries of radioactivity by Becquerel and X-rays by Roentgen at the end of the nineteenth century and the experiments of Rutherford early in this century, the prophecy of Boyle and the hopes of the alchemists had been realized. Lawrence saw even greater potentialities in the exploitation of the immensely more powerful agents available from artificial radioactivity and man-made accelerators and was eager to see them applied. For this purpose, he had another, Dr. John Lawrence in the possibilities of the neutron as a therapeutic agent and had assigned P. C. Aebersold, then a graduate student, to help him to establish the physical and radiological procedures involved. A small beginning had already been made in the use of the radioactive isotopes of phosphorus, sodium, and iodine as tracers in biological research. To facilitate a rapid development of such researches both at Berkeley and elsewhere, I was asked to assume responsibility as staff chemist to develop procedures whereby target materials could be bombarded, processed, and delivered in forms suitable for direct applications in biological systems. The problems involved were sufficiently challenging and urgent so that from the early months of 1937 until well into 1940, most of my energies were channeled into this activity.

Almost immediately, I found it necessary to devise a procedure for rapid and reproducible preparation of the 21 min ^{11}C, for use by S. Ruben, W. Z. Hassid, and I. L. Chaikoff in some researches in which they proposed to investigate carbohydrate metabolism by means of ^{11}C-labeled sugars prepared photosynthetically from $^{11}CO_2$. (See Figures 1–3.) In a short time, it became apparent (*14*) that B_2O_3 powder, bombarded by deuterons in a special external target chamber designed by Kurie, evolved much of the ^{11}C produced in the $^{10}B(^2H,n)^{11}C$ reaction as $^{11}CO_2$. The success of this procedure which eliminated hazardous radiation exposure incidental to manipulation of target material, expedited the researches sufficiently so that Ruben was encouraged to initiate researches on photosynthesis itself—an undertaking into which I was soon drawn full time outside of my duties as radiochemist.

In the meantime, Ruben observed in May, 1938, that a number of graphite targets, which I had been using to make ^{13}N by the $^{12}C(^2H,n)$ reaction for some researches on nitrogen fixation (*15*), contained no residual long-lived activity isotopic with carbon. He concluded that any ^{14}C formed by the $^{13}C(^2H,^1H)$ reaction with a half life of up to 200 years could have been detected. This finding underscored the probability that ^{14}C, if it existed, was a short-lived isotope.



External target for C^{11} production. Assembly on the right contains window and main chamber. Middle section shows B_2O_3 target material. This section was clamped into the main section so that the whole constituted a closed system cooled by the water pipes shown. The B_2O_3 powder was held to the target plate by a frame and window assembly (parts shown on left). The target, as shown, had just survived bombardment with 30–50 μamps of 7–8 Mev deuterons for 20 minutes.

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My constant exposure to cyclotron targets kept me in a steady state of radioactive contamination which rendered me *persona non grata* around radioactivity assay equipment. I recall, as an example, an experience during a collaboration with Philip Abelson sometime in late 1937 when we were attempting to use an apparatus consisting of an ionization chamber connected to an FP-54 Pliotron tube amplifier. We were harassed by occurrence of an eccentric and irregular background drift of variable magnitude. Finally, Abelson noted that the effect was correlated with my movements toward and away from the apparatus. While I stood in a corner, he systematically stripped me and established that the disturbance originated from the front of my pants. Likewise, in my collaboration with Ruben, it was necessary to keep me away from the counting equipment. In our researches, we came to a logical arrangement whereby Ruben assumed sole responsibility for assay and I concentrated on tracer isotope production.

I cannot leave this section of my presentation without mentioning that Ruben was responsible, almost single-handedly, for the growth of interest in tracer methodology which occurred at Berkeley in the years 1937–8. His unique combination of experimental skills, energy, wide-ranging interests, and quick grasp of essentials when confronted with new and unfamiliar areas of science, provided a focus for the efforts of an ever-increasing number of able investigators.

By the middle of 1938, the demands for cyclotron time made by biologists and clinicians was so great that it was mandatory to initiate round the clock operation of the cyclotron—by now a 37-in. machine. In addition the pressure to build bigger machines had impelled Lawrence to seek additional subsidies from biologically oriented foundations as sources likely to support such projects. As an argument, Lawrence cited preliminary results obtained with neutron therapy and by applications of radioactive isotopes, such as ^{24}Na, ^{32}P, and ^{59}Fe, in medical diagnosis. A 60-in machine was almost ready for operational tests and further development depended critically on favorable responses from medically and biologically oriented sources of funds which had been solicited. Added urgency was generated by the demonstration that ultimate energies and ion currents were likely to be far in excess of the limits earlier thought to be reasonable.

The researches of R. R. Wilson in this period were of considerable importance in pointing the direction for further developments of cyclotron design. Wilson showed that very large beam currents at energies somewhat lower than those emergent in the external target area circulated inside the accelerating electrodes (*16*). He realized that if a means could be devised to use these internal beams, bombardments of much greater magnitude than those possible with external targets could be effected. Moreover, he was able to show that a large fraction of the internal circulating ion current could be intercepted by appropriately designed "probes" without appreciable diminution of external beams. However, the problems which arose in the achievement of acceptable internal targets were formidable and sufficiently difficult to discourage immediate efforts to exploit the internal ion currents. As an example, the external beams of 7–8 Mev and 50–100 μamp required dissipation of 300 to 800 watts—a power input which, even with well cooled targets of good heat conductance, required sequestration of target material from the cyclotron vacuum by the use of aluminum or other metal foil windows. Internal beams with ion currents as much as several milliamperes and energies only slightly less than 6–7 Mev, generated power inputs of an order of magnitude greater than those associated with the external beams.

However, the cyclotron was increasingly unable to keep up with the demands for radio-isotopes, as well as for bombardment time for clinical trials; even the enforcedly modest needs for essential nuclear physical research could not be satisfied. This led Wilson and me to try to devise acceptable internal targets for radio-isotope production—an enterprise in which we succeeded late in 1938. This research was to prove the turning point in the sequence of events comprising the prenatal history of ^{14}C. In fact, as we remarked at that time (*17*),

> Obviously, the method of internal targets should find its most important application in the preparation of radio-isotopes which are long-lived and difficult of activation, as well as in the demonstration of the existence of many radio-isotopes as yet undiscovered.



The author preparing a B_2O_3 target.

The Final Phase, 1938–40

The search for funds proceeded with some success through 1938 and into 1939, so that both cyclotrons were in operation on a full schedule when the discovery of nuclear fission burst on the world in January, 1939. In the meantime, the ambitions of Lawrence to produce an even greater machine had been spurred by the successful operation of the 60-in. cyclotron. He pressed for more support from the same biologically-oriented sources he had tapped previously, on the basis of the considerably expanded collection of clinical data as well as the enormously developing tracer program at Berkeley and elsewhere which was made possible by the Berkeley cyclotrons.

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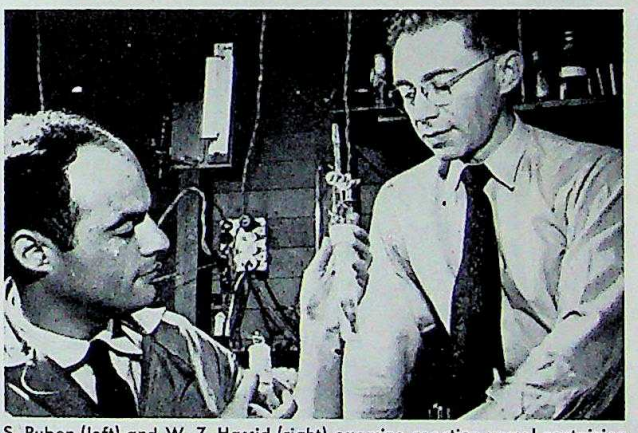
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In our own researches on photosynthesis, ^{11}C had by this time been exploited to its ultimate limits (*18*).

As an example of our difficulties, we had found it essential to try an ultracentrifugal determination of the molecular weight of the labeled intermediates produced during photosynthesis in the presence of $^{11}CO_2$. The necessary apparatus was at Stanford University, 50 miles away from the Berkeley cyclotrons through heavy traffic. We calculated that it would be possible to make the $^{11}CO_2$, incubate algae with it, extract the resultant intermediates and drive to Stanford. There would be insufficient time, however, to do a proper centrifuge run. We considered a number of possible courses of action, such as arranging a police escort for the motor trip to Stanford, posting one of us at Stanford to have the counting apparatus ready, etc., but one night a brilliant solution occurred to Sam Ruben. He woke me at 2 A.M. to suggest carrier pigeons!

Fortunately, this problem was finally resolved by the discovery that an apparatus identical with that at Stanford was available at the Shell Oil Company research laboratories only 10 min drive from the cyclotron. Even with this dispensation, we found it impossible to obtain the precision needed to establish with certainty the average size of the early intermediates in photosynthesis.

In a gloomy conference late in September, 1939, Ruben and I reached the conclusion that without a long-lived isotope of carbon our researches were at an end. I suggested one last desperate try to make ^{14}C by means of the internal target technique. The difficulty was that, in view of the pessimism about the probability of a long-lived isotope, it was not possible to liberate any of the internal targets from their constant use for production of ^{32}P and ^{59}Fe.



S. Ruben (left) and W. Z. Hassid (right) examine reaction vessel containing C^*O_2 and photosynthesis leaf system.

It was with some amazement therefore, that I found myself shortly after this conference being told by Lawrence that both cyclotrons must be diverted forthwith to a full time effort to make sure that long-lived isotopes of hydrogen, carbon, nitrogen, and oxygen did, or did not, exist. The reason emerged soon. During Lawrence's most recent efforts to ensure increased and continued subsidies for further cyclotron development, he had found that some doubts had been raised as to the real value of radioactive isotopes in biological research, relative to the rare stable isotopes, such as ^{2}H, ^{13}C, ^{15}N, and ^{18}O. Thus, while these very useful stable isotopes existed as tracers for the elements of primary importance in biology, there were no comparable radioactive isotopes with reasonably long life-times available; i.e., no radioactive hydrogen isotope existed (it was thought that tritium was stable relative to ^{3}He), the carbon isotopes ^{10}C and ^{11}C were limited by their half lives of 8 sec and 21 min, respectively, and only very short-lived ^{13}N and ^{15}O were known for nitrogen and oxygen.

Lawrence asked me to organize a complete and systematic campaign to probe every possibility for the existence of long-lived isotopes anywhere in the first row of the periodic table—but especially for H, C, N, and O. From the experience gained in previous years, it was a simple matter to draw up a comprehensive plan which included a detailed set of protocols for every nuclear reaction possible with the projectiles available, including the choice of target materials and target chemistry. It was natural to concentrate first on carbon. An abridged plan taken from my notebook, as drawn up in September, 1939, is shown in Table 1. Similar plans were devised for nitrogen and oxygen activities based on bombardments of B_2O_3, graphite, BN and $(NH_4)_2F_2$ targets. Every possibility was assumed—even that there might be long-lived isomers of stable nuclei (e.g., ^{12}C, ^{13}C) or of short-lived nuclei (e.g., ^{13}N, ^{15}O).

The first trials involved bombardment of B_2O_3 with 16 Mev alpha particles in the 37-in. machine (Sept. 27–29). A 5 μamp hr exposure yielded no long-lived activity in the gas space, assayed by direct introduction of the target gases into an ionization chamber-pliotron apparatus. The residual powder was burned with a small bit of filter paper as a carbon carrier, but the resultant gases were also inactive. It could be concluded that the 16 Mev alpha particles were inadequate to produce significant quantities of ^{13}N, ^{14}N, ^{13}C, or the isotope ^{14}C by means of the $(^{4}He,n)$ or $(^{4}He,^{1}H)$ reactions. Next, B_2O_3 was bombarded for 34 μamp hr with 16 Mev deteurons in the 60-in. machine. In this experiment, E. Segré collaborated and examined the

Table I. Plan—Production Reactions for Possible Long-Lived Carbon Isotope, September, 1939

Reaction[a]	Target material	Target chemistry
$^{9}Be(^{4}He,n)C^{12*}$	BeO (atmosphere 3% CH_4 in O_2)	Collect C^*O in gas, burn residue to CO_2, with carrier C
$^{10,11}B(^{4}He, {}^{1}H)^{13*,14}C$	B_2O_3 (" " ")	" "
$^{11}B(^{1}H, \gamma)C^{12*}$	" (" " ")	" "
$^{11}B(^{2}H,n)C^{12*}$	" (" " ")	" "
$^{12,13}C(^{2}H, {}^{1}H)^{13*,14}C$	Graphite (" " ")	" "
$^{14,15}N(n, {}^{1}H)^{14\ 15}C$	Ammonium nitrate (nitrate)	Aspirate CO_2-free air through solution, burn emergent gases and trap C^aO_2

[a] Energies available: protons (4-8 Mev), deuterons (8-10 Mev), alphas (16-32 Mev).

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activities produced in the gas phase which were introduced again directly into an ionization chamber detector. He found the expected ^{11}C in enormous quantities and also an activity with a half life of 112 min. Unfortunately, we traced this to ^{18}F produced by the (^2H,2n) reaction on ^{18}O. By October 16, 1939, I had reached the conclusion that none of the alpha particle induced reactions were feasible—it appeared that at least 5×10^5 μamp hr of 32 Mev alpha particles would be needed to produce one μcurie of radioactivity with $t^1/_2$ ~1–3 hr.

On October 17, I tried exposure of methane to 20 μamp hr of 16 Mev deuterons in the 60-in. machine and obtained only the expected ^{13}N (several hundreds of millicuries), ~0.01 μcurie of ^{18}F from a small amount of contaminant oxygen, and again no long-lived activity.

In the meantime, I had begun continuous exposure of a graphite probe target introduced through the north port of the 37-in. machine. This probe was allowed to collect stray deuterons in the internal cyclotron beam for nearly a month throughout January, 1940. The probe was inserted so as to intercept practically all deuterons during night operation and retracted to allow normal operation in the day. I undertook the night bombardments, aided occasionally by others who needed the copious supply of neutrons produced for further studies on the uranium fission reactions. The probe target was not designed properly to withstand intense bombardment. I had merely smeared colloidal graphite on the water-cooled copper surface and counted on replacement during frequent inspections of whatever graphite was found to be blasted off. The weather was unusually violent, even for January, and most nights witnessed heavy drenching rains and wind storms. The noise of the rain on the laboratory tin roof, interspersed with cannonades from cyclotron high-voltage discharges created an appropriate fanfare for the birth of ^{14}C which was fated to come during this bombardment.

This experiment had been regarded as the most likely to make ^{14}C. It was performed with mixed desperation and resignation, and involved considerable hazard from radiation exposure as it was necessary to examine the intensely radioactive probe nightly to insure that some graphite still clung to the target surface. Occasionally, I found the irradiated graphite almost on the verge of flaking off and so had to cement it back on with more graphite.

On February 15, during a particularly violent storm, I terminated this bombardment which had involved exposure of the graphite to 5700 μamp hr of 7–8 Mev deuterons. Shortly before dawn, I left the graphite, which looked like bits of gravel, in a weighing bottle on Ruben's desk. On the way home to get some sleep for the first time in several days, I must have presented a sorry spectacle—unshaven, red-eyed and dazed—for I was intercepted and questioned by police looking for an escaped convict who had committed several revolting murders earlier in the evening. Fortunately, I failed to pass muster and was released to continue stumbling onwards to sleep.

On awakening some hours later, I phoned Ruben who had found the sample, burned it to CO_2, precipitated it as $CaCO_3$, and noted some activity when he examined the precipitate inside a screen-wall counter of a type designed by W. F. Libby (*19*) to permit assay inside the sensitive volume of a Geiger-Müller tube. No activity could be detected with the usual thin-walled tubes. The effect was very small—about four times the counting background—but reproducible. In some excitement, I hurried back to the laboratory, prepared a new probe target made up of graphite solidly bonded to copper and then joined Ruben to press on further with the identification of the activity. By Tuesday afternoon, February 27, we had disposed of the last uncertainty—that the activity might have arisen from ^{35}S produced by the (^2H,^1H) reaction on the sulfur as a possible contaminant of the graphite used—but had left only about ~$^1/_8$ of the original activity. We wrote a preliminary account for publication as a letter and later as an abstract in the *Physical Review* (*18*), and on Wednesday evening motored to Lawrence's home to acquaint him with the result. Lawrence was resting in an attempt to banish a cold before his appearance the next night, Thursday, February 29, to receive the Nobel Award in Physics. His pleasure was unbounded and shook our own certainty as we revived nagging doubts about the reality of the activity we were ascribing to ^{14}C. After all, it was only an activity half of the counting background when counted as solid $CaCO_3$ even though it had persisted through repeated cycles of precipitations with $CaCO_3$ and acidification to CO_2. It was a comfort to realize that, of all the elements in the periodic system, only carbon possessed an oxide which could be liberated repeatedly from acid solutions under oxidizing conditions—a fact which ensured that the activity observed was in fact isotopic with carbon.

The new probe target, with its improved mode of bonding, withstood much more intense probe beams, so that in a week it had accumulated 13,500 μamp hr of exposure to 3–4 Mev deuterons on a probe inserted in the south port of the 37-in. machine. The activity obtained was 10–20 times counting background and sufficient to establish the isotopic assignment as ^{14}C, to show that the beta-energy maximum lay in the neighborhood of ~120 kv, and that the half life was certainly greater than 20 years. I was able to make an estimate for $t^1/_2$ based on the following considerations. The first probe sample, after 5700 μamp hr, had shown a total activity of ~100 disintegrations sec^{-1}. From a knowledge of the cross section at 3–4 Mev for the reaction $^{12}C(^2H,^1H)^{13}C$ and the assumption that the cross section for $^{13}C(^2H,^1H)^{14}C$ was similar, it could be calculated that the ratio of ^{14}C nuclei made to deuterons stopped in the graphite would have been ~1/60,000 assuming 100% ^{13}C or $[1/(6 \times 10^6)]$ for the graphite which had the normal isotope content of 1% ^{13}C. The total number of deuterons was $\sim 1.2 \times 10^{20}$ (5700 μamp hr), hence the number of ^{14}C nuclei produced ($N_{^{14}C}$) was $(1.2 \times 10^{20}/6 \times 10^6)$, or 2×10^{13}. Knowing $N_{^{14}C}$ and $dN_{^{14}C}/dt$ (100 dis/sec), it was simple to deduce the $t^1/_2$ as $\sim 4 \times 10^3$ years! This value was remarkably close to the true disintegration half life of ~5700 years determined many years later, but the agreement was quite accidental, as this 1940 estimate was uncertain by as much as an order of magnitude in either direction. However, it did shed light on the

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reason for the negative results of previous years—the half life of ^{14}C was too great to permit production in significant quantities until the internal target technique had been developed so that bombardments of 5000 μamp hr and upward were possible. Moreover, it was clear that ^{14}C had an enormously long half life—a result most surprising on theoretical grounds, as remarked previously.

In all of these exercises, the basic assumption was that the $(^2H,^1H)$ reaction on ^{13}C would be much the most likely to succeed. This type of reaction exhibited the largest cross sections among those excited by charged particles, and had the advantage that target chemistry was simple and dilution of isotopic material minimal. The reaction of slow neutrons with ^{14}N, which had led to the initial postulation of ^{14}C, was regarded as a possible, but not promising, process as a basis for ^{14}C production. It may come as a surprise to many of you that this impression prevailed in 1940 in view of the fact that the $^{14}N(n,^1H)^{14}C$ reaction is the method of choice now.

There were many cogent reasons for neglecting the slow neutron reaction. First, the neutrons produced in the cyclotron were not primaries, but secondary particles with ranges up to many meters in dense media so that only a fraction could be captured by ^{14}N nuclei, even with the best possible geometry. On the other hand, all deuterons produced as primaries with very small ranges could be absorbed in a minimal amount of target. Second, cross sections for slow neutron capture were high only for the (n,γ) process with which the $(n,^1H)$ process was expected to compete poorly. Thirdly, the recoil ^{14}C nuclei produced would not be expected to reach equilibrium in chemical species sufficiently uniform to permit simple, efficient extraction. Nevertheless, two carboys, each containing 5 gal. of saturated ammonium nitrate solution were placed near a good source of neutrons—the deflector region of the 60-in. cyclotron—in January. Prior to exposure, the solutions were acidified with dilute nitric acid, aspirated with CO_2-free air to remove contaminant carbonate, which would dilute excessively any radioactive carbonate formed (not that we expected to see any!), and sealed tightly. The success with the graphite probes had quite completely distracted my attention from these carboys, and I was busily engaged in an attempt to improve the $(^2H,^1H)$ yields by fabrication of ^{13}C enriched graphite probes when an angry deputation from the 60-in. cyclotron paid me a visit and issued an ultimatum to remove the carboys, which had sprung leaks and were proving an intolerable nuisance. The deflector region was in constant need of attention for deflector adjustments; and the cyclotron crew was weary of the constant pushing and pulling to move the box, especially a box wet with acid, to get at the deflector controls.

So, with no great enthusiasm, I went over to the 60-in. cyclotron with a cart and moved the box to Ruben's laboratory in a ramshackle hut, affectionately labeled the "Rat House." Ruben and I decided to make a gesture and aspirate some air, freed of CO_2 by passage through soda lime, through the carboys in the hopes some ^{14}C might be entrained and removed as $^{14}CO_2$. A copious precipitate of $CaCO_3$ which formed in the $Ca(OH)_2$ trap after passage of the effluent gases through a combustion train lent no encouragement, as it indicated large quantities of CO_2 had diffused into the ammonium nitrate solutions and that any activity formed was likely to have been lost because of excessive dilution. To our astonishment, we found that a small fraction of this precipitate was so active it completely paralyzed the screen wall counter! In a short time, we ascertained that we had several microcuries of ^{14}C—a quantity two or three orders of magnitude greater than any we had seen from the probe bombardments. Needless to say, our interest in the $^{13}C(^2H,^1H)^{14}C$ reaction vanished, never to return.

Where had I gone astray in denigration of the slow neutron process? All the assumptions about poor cross-sections and complex target chemistry were eminently sound and eminently wrong! As it developed later, the $(n,^1H)$ process for ^{14}N was favored heavily over the (n,γ) process—possibly the only exception to the general rule. It is remarkable that the only other instance of appreciable yield from $(n,^1H)$ process with slow neutrons also involves production of an important radioactive tracer (*20*)—^{35}S from the $(n,^1H)$ reaction on ^{35}Cl. Moreover, as we found in further experimentation (*21*) and as was later confirmed by P. E. Yankwich, T. H. Norris and G. K. Rollefson (*22*), well over 80% of the recoil ^{14}C found its way into the volatile oxides of carbon (CO and CO_2) and so made possible a simple, practically quantitative recovery of the ^{14}C from any amount of bulk solution. The realization of all these facts caused some talk shortly thereafter of a syndicate to build a battery of cyclotrons designed solely for ^{14}C production.

In the meantime, Lawrence authorized construction of a special set of stainless steel cans with aspirator inlets and outlets to be mounted as a permanent shield around the 60-in. cyclotron. This set-up was expected to produce hundreds of microcuries of ^{14}C monthly. After these cans had been in place a month, however, worries about ammonium nitrate solutions as a possible explosion hazard, however remote, induced Lawrence to order them removed. A few years later, in 1944, these cans were to serve as a source of ^{14}C in the first published tracer researches with ^{14}C, carried out in collaboration with Dr. H. A. Barker (*23*).

The story of the birth of ^{14}C ends here. But, of course, there were many other chapters to come, e.g., the expansion of ^{14}C production from the microcurie to the curie level which followed the development of nuclear reactors, and the resultant proliferation of ^{14}C as a tracer isotope in every area of biological research. Another chapter—which ties into a last thread from the early history up to 1940—concerns what may prove of great significance in the future of nuclear theory, namely, the anomalously low rate of ^{14}C decay. All through the period from 1938–40 the search for ^{14}C was conducted under a cloud of certainty that the half life of ^{14}C was probably in the order of seconds, or less. When it was seen by July of 1940 that the half life of the material we had produced was certainly of the order of years, in fact millenia, active doubts were expressed that the activity observed was isotopic with carbon. Even the testimony of algae, which absorbed the activity photosynthetically, and the chemical behavior of the activity failed to still these doubts at the

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time! The question raised—why ^{14}C?—remains with us today.

Explanations have been offered *seriatim:* first, that there is a change in parity, secondly, that ^{14}C is wholly $^1S_0$ and ^{14}N purely ^3D, so that a transition between them is ΔL forbidden: thirdly, there is a fortuitous cancellation in the matrix element for decay (*24*). The last suggestion is favored at present (*25*) but is not wholly acceptable. The first two are definitely excluded on experimental as well as theoretical grounds (*24, 25*). It is apparent that the riddle of ^{14}C decay implies an answer which should be an important part of the future history of nuclear theory. In conclusion, I quote as a moral for our story, the words of the late psychiatrist, E. Winzholz—"We never let our theories interfere with our practice."

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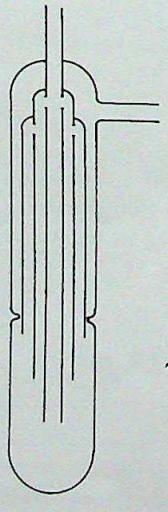
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High Capacity Vapor Traps

Vapor traps used in vacuum systems are usually designed for efficient freezing out of traces of vapor. Less common applications are encountered in solid-vapor-solid distillation processes such as the "freeze-drying" of solutes or suspenoids. Conventional traps, when built to convenient dimensions with glass, have insufficient capacities for this purpose.

A "cold-finger" type trap is compact and easy to make. The conventional "cold finger" will clog within the tip of the central core if the radius of the core is very much smaller than that of the outer cylinder. If the radius of the central core is made progressively larger, a situation will ultimately prevail in which an ice mass between the outer cylinder and the central core clogs the trap. In either case the total volume of solvent which may be distilled prior to clogging is severely limited.



The modified cold-finger diagrammed in the drawing has a core made of three concentric cylinders with ports connecting the space between each cylinder. The outside diameter of the trap is 6 cm. The ports are located near the top of the core so that the heat flux from the atmosphere keeps them free of condensate. There are three alternate paths for the vapor. The trap cannot clog until all three paths have been completely blocked. Futhermore there is a large ice collecting area over which the vapor intake is distributed. The capacity of the trap is about 165 ml of water prior to clogging.

The trap construction cost was $18, a small fraction of the cost of commercially available freeze-drying traps made from stainless steel.

This work was done while the author was a Summer Research Participant in the Chemistry Department of the University of Buffalo, sponsored by the National Science Foundation G-15159. Mr. Joseph West fabricated the trap prototype and contributed valuable suggestions for the basic design.

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Demonstration of Radioautography and Paper Chromatography Using a Polaroid Camera

A simple combined demonstration of paper chromatography and radioautography illustrating the separation of two ^{14}C-labeled amino acids has been devised. The experiment takes approximately three hours to perform and is suitable either for classroom demonstration or as a laboratory exercise. With the exception of the Polaroid camera, the experiment requires relatively simple equipment and makes use of *license-free* packages of inexpensive labeled amino acids. At the completion of the experiment, the student may examine both the positive print of the radioautograph as well as a ninhydrinsprayed paper chromatogram.

A model 800 Polaroid camera is used for the exposure, development, and printing of the radioautograph. Other models of Polaroid camera may be substituted. However, the size of the chromatogram and the card (Fig. 2) used for mounting the chromatogram must be adjusted accordingly. The choice of such a camera stemmed from its availability as part of a photographic reproduction unit, and its use obviated wet development necessary for the usual no screen X-ray film. Obviously without the camera or suitable holder, the experiment cannot be performed.

PolaScope/Type 410 film is employed because of its high A.S.A. rating (10,000) and panchromatic nature. Type 47 film (A.S.A. rating 3000, an orthochromatic film) can be used but requires longer exposure times.

Ten μc each of lyophilized *d,l*-aspartic acid-4-^{14}C and *d,l*-alanine-1-^{14}C are needed. The contents of each vial is dissolved in 0.20 ml distilled water. It is necessary to warm the aspartic acid to achieve solution. The specific activities of the amino acids should be of moderate value (approximately 1 mc./*mM*) in order to obtain enough of the amino acid on the chromatogram to be detected by the ninhydrin spray.

Whatman No. 1 Filter Paper, is cut to size as in Figure 1. An 800 ml beaker serves as the chromatographic chamber. A piece of "Saran Wrap" is used to cover the beaker and is held in place securely with rubber bands.

Chromatographic solvent: *n*-butanol, glacial acetic acid, water (40:10:60) mixed. Allow phases to separate and use upper phase.[3]

Ninhydrin spray: An aerosol of ninhydrin in ethanol and freon was used.[4]

A small oven set at 65–70°C serves for running of the chromatogram at elevated temperature in order to speed the time required for achieving separation as well as improving resolution. The oven is also used for drying the chromatogram or heating it after spraying with ninhydrin.

Preparation of the Chromatogram. Five μl (.25 μc) of solution are used for each spot. Three spots are made at the origin (see Fig. 1), one of alanine, one of aspartic acid, and one containing 5 μl of both solutions. After the spots are placed on the paper, the chromatogram is set into the beaker and held in place by folding the "ears" over the edge of the beaker. The chromatogram should hang vertically and not touch the bottom or sides of the beaker. Trim the bottom edge if necessary. Add 30 ml of the solvent mixture, and cover the beaker with a square of Saran Wrap (approximately 10 in. × 10 in.). Fasten in place by means of a rubber band. At this time, the chromatogram is again checked for position, and can be moved slightly by pressing one or both "ears" to straighten it and insure even movement of the front. The preliminary preparation just described takes something less than one hour.

The beaker thus prepared is now ready to be placed in a preheated oven at 65°C for one hour. During this time, a mounting card for the chromatogram is prepared. A 4- × 6-in. index card is used for this purpose. It should be marked with pencil as shown in Figure 2.

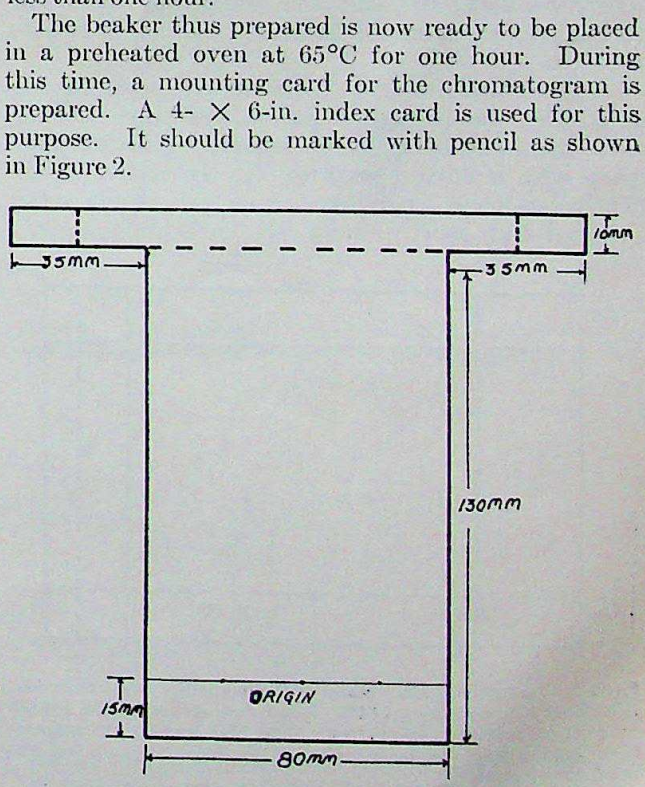


Figure 1. Diagram of the paper chromatogram. Fold along dotted lines.

[1] Supported in part by National Institutes of Health Grant B-2453.

[2] Generously donated by the Volk Radiochemical Co., Skokie, Illinois. These may be purchased in license-free quantities at nominal prices.

[3] Slotta, K. H. and Primosigh, J., *Nature*, 168, 696 (1951).

[4] Obtained from the Sigma Chemical Co., St. Louis, Mo.

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The Radioautogram. When the chromatogram is removed from the oven, the chromatogram is immediately removed and the front is marked with pencil. If a hood is convenient it is preferable to do this operation there. However, by removing the chromatogram rapidly and recovering the beaker, the noxious fumes of the solvent are held to a minimum. After drying for a few minutes (in air or in the oven) the front and origin lines are marked with two spots each of a solution of methyl orange in 0.1 ml of the alanine solution already prepared. (Any other radio-labeled compound will serve as well. Only a few crystals of methyl orange suffice to color the solution.) The "ears" may be cut off or folded under before the chromatogram is taped in the central rectangle on the 4- × 6-in. card (Fig. 2.).

The card is now ready to be placed in the camera. Before inserting the film in the camera, the card is placed in the focal plane of the camera with the folded end extending over the edge of the base nearest the film compartment. If the end is not thus folded, when the film is inserted and pulled across, it may be damaged by the edge of the card. The chromatogram is facing up so as to come into direct contact with the film when it is pulled across. The film is placed in the camera and pulled through to place it in position. After one hour, the film is pulled through once again and the photograph removed after 10 seconds. A typical radioautogram of aspartic acid and alanine is seen in Figure 3.

Chromatographic Separation Demonstrated by Ninhydrin. The card is now removed from the camera. (This must be done in a dark room or under a photographer's cloth so as not to ruin the remaining film.) The chromatogram is removed from the card, sprayed with ninhydrin, and heated in the oven, or over a hot plate. In a few seconds blue and purple spots will appear matching perfectly the radioautogram. This part of the demonstration takes less than 5 minutes to complete.

The ninhydrin detection, if desired may be performed on another chromatogram run at the same time in order to avoid opening the camera. Aspartic acid reacts with ninhydrin spray to give the typical initial blue color which is different from the purple color observed with most amino acids [including alanine]. Both amino acids are illustrated in this experiment. Both ninhydrin "spots" and radioautograph "spots" should correspond in R_f values as well as in size and shape. The student may calculate R_f's for both the chromatogram and radioautogram.

The elevated temperature used for developing the chromatogram improves separation of the alanine and aspartic acid as well as permitting shorter development time. A radioautogram of a paper chromatogram developed at room temperature for 90 minutes is illustrated in Figure 3*b*.

The exposure time of the chromatogram to the 410 film may be cut in half if time is of importance. However, over-exposure ruins the definition of the spots, but does bring into view the presence of radioactive impurities. This may be demonstrated by leaving the chromatogram in contact with the film overnight or longer if possible.

For a laboratory exercise approximately thirty chromatograms may be run from 10 μc samples each of alanine and aspartic acid. If it is desired to mark the front and origin of the chromatogram prior to exposure to the film, an additional vial of radioactivity is required.

A laboratory exercise of this experiment is limited by the use of the camera. If each student (or group of students) is to obtain a radioautograph of his chromatogram, a half hour's exposure works well. However, this means that the camera must be loaded and unloaded in a dark room or under a dark cloth without unduly disturbing the position of the film. With a little practice this can be easily done. A single roll of film yields eight exposures, but the time for exposing all chromatograms for a laboratory exercise will involve a considerable amount of time.

Although the use of these quantities of radioisotopes is license exempt and represents virtually no danger to the user, pedagogically it is wise for the instructor to practice principles of proper handling techniques of radioisotopes.[5]

[5] RADIN, N., edit., "Radioisotope Experiments for the Chemistry Curriculum," Chap. 2. (Obtained from the Nuclear-Chicago Corporation, Des Plaines, Ill.)

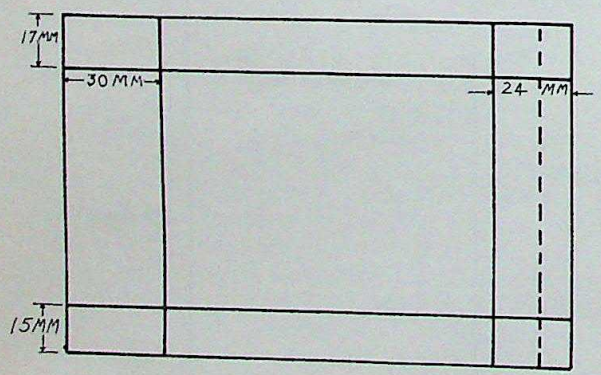
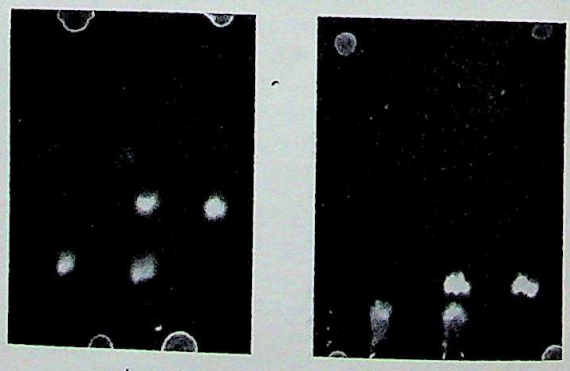


Figure 2. Card used to mount paper chromatogram for exposure to film in the Polaroid camera, model 800. Mount chromatogram in the central rectangle and fold card along the dotted line. The card must be mounted in the focal plane of the camera such that the folded edge fits into the sensitive film receptacle.



A B

Figure 3. (*A*) Radioautogram, developed at 65°C (from left to right: ^{14}C-aspartic acid, ^{14}C-aspartic acid + ^{14}C-alanine, and ^{14}C-alanine). The irregular spots noted on the upper and lower margins are the front and origin line-markers. (*B*) Same, but developed at room temperatures.

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Vibration-Rotation Spectrum of HCl

A physical chemistry experiment

Spectroscopy, a technique commonly used in many areas of chemical research, permits the determination of molecular parameters to a very high degree of accuracy. The molecular spectroscopy experiment described below is performed in the undergraduate physical chemistry laboratory. Parts of the experiment may be omitted without damaging its value if spectra of adequate resolution are not obtainable. In its complete form, the experiment yields such molecular parameters as the interatomic distance, the vibration frequency and the anharmonicity constant, and also such macroscopic properties as the "rotational" temperature, dissociation energy, the free energy function and the heat capacity.

The Experiment

The sample of gaseous hydrogen chloride is prepared by mixing a few drops of concentrated sulfuric and hydrochloric acids in a ten-cm *quartz* sample cell. The sulfuric acid dehydrates the constant-boiling hydrochloric acid producing HCl gas. DCl, if desired, is prepared from D_2O.

Two absorption spectra are used: that of the ($v' = 1 \leftarrow v'' = 0$)[1] band between 3.3 and 4.0 microns, and that of the ($v' = 2 \leftarrow v'' = 0$) band between 1.7 and 1.85 microns. Either spectrum, with the rotational lines resolved, is sufficient for the bulk of the experiment. In practice we have used the Beckman IR-5 or Baird AB-2 infrared spectrophotometers at 3.3μ, and the Cary model 14 at 1.7μ. The 1.7μ spectrum has been observed also with a Beckman DK-2 but the resolution obtained is sufficient to give only the 0′-0″ line. New IR grating instruments now coming onto the market offer adequate resolution at low cost and promise to be widely available.

Data

The (1′-0″) spectrum at 1.7μ taken with the Baird AB-2 is shown in Figure 1. Normally this is used only to obtain the (0′-0″) line; however, the spectrum shown has been interpreted to give an interatomic distance.[2] Resolution comparable to that of Figure 2 may be obtained with the more modern grating instruments.

The (2′-0″) spectrum taken with the Cary 14 is shown in Figure 2. The general features are the same as those of Figure 1, except that there is much greater resolution: the individual rotational lines are clearly seen and are labeled $R(0)$, $R(1)$, etc. Of each pair of lines, the more intense member is due to $H^{35}Cl$, the less intense to $H^{37}Cl$.

The features of the resolved spectrum may be related to the molecular structure. Figure 3 shows potential energy as a function of the interatomic distance r. Vibrational levels are shown as the horizontal lines. The 1.7μ spectrum results when the molecule in the 0 level absorbs light and goes to the 2nd level.

Details of these levels are shown in Figure 4. In addition to the vibrational energy, the molecule also has rotational energy $F(J)$ given by

$$F(J) = J(J+1)B_v \qquad (1)$$

where J is the rotational quantum number and B_v is the rotational constant equal to $h/8\pi^2 I_v c$ where I is the moment of inertia, μr^2. Figure 3 shows that r must be

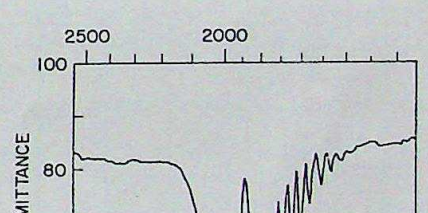


Figure 1. The fundamental (1′ ← 0″) spectrum of HCl under low resolution—per cent transmission versus wavelength in microns.

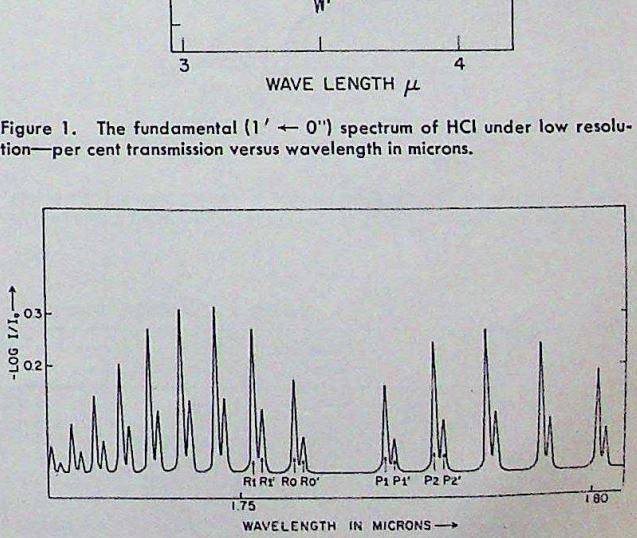


Figure 2. The first overtone (2′ ← 0″) spectrum under high resolution—log I_0/I versus wavelength in microns. The lines in the P and R branches are labeled prime (′) for $H^{37}Cl$ and un-prime for $H^{35}Cl$.

EDITOR'S NOTE: This paper and the one that follows are part of a series designed to provide work suitable for training undergraduates in the interpretation of chemical phenomena in terms of molecular energetics. See also THIS JOURNAL, 39, 626 and 630 (1962).

[1] The single prime in such a notation signifies the upper vibrational state, while the double prime signifies the lower vibrational state. This convention is followed throughout this article.

[2] From private communication with B. W. Ristow, r (obtained) = 1.28 Å, r (literature) = 1.275 Å.

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larger for the higher vibrational states studied; therefore $B_{v=2}$ must be smaller than $B_{v=1}$. The J value for a transition may change only according to the selection rule:

$$\Delta J = \pm 1 \qquad (2)$$

The resulting transitions are shown as vertical arrows and the resulting spectral lines are shown below. The high energy part of the spectrum ($\Delta J = +1$) is called the R branch; the low energy part ($\Delta J = -1$) is called the P branch. Each line is labeled $R(0)$ . . . or $P(1)$ . . . , according to the J value of the lower level involved.

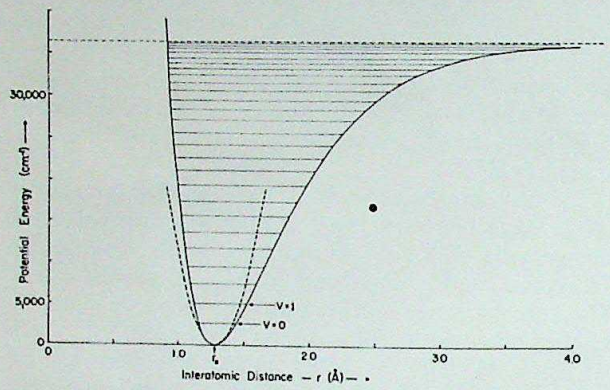


Figure 3. Potential energy curve: the dashed line is the harmonic oscillator (parabola) approximation. The vibrational levels are drawn to scale.

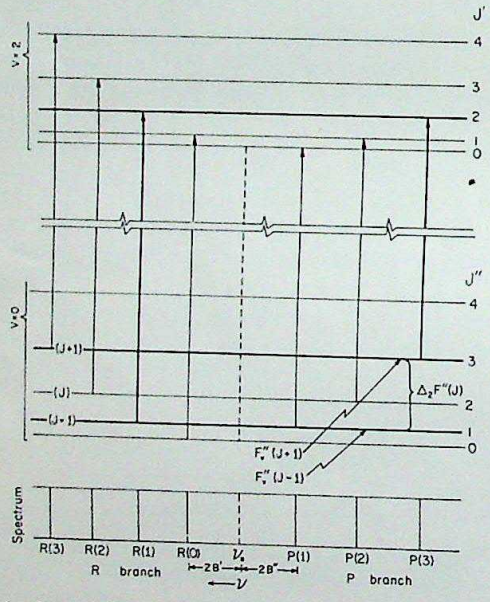


Figure 4. Details of the vibration-rotation transitions showing the origin of the P and R branches. $B_{(v=2)} < B_{(v=0)}$, hence the band is shaded to the red.

Figure 4 shows that because B' (upper level) $> B''$ (lower level) the spacing between spectral lines becomes larger as one goes to lower energy from the R to the P branches. This is called "*shading* to the red." If the temperature were great enough so that higher rotational levels were populated, it would be observed that the R lines eventually would fall one upon the other; this is called a band "head." In transitions between *different* electronic states we have also $B_{v'} = B_{v''}$ or $B_{v'} < B_{v''}$. In the former case the lines are equally spaced; in the latter, the spectrum is "*shaded* to the violet." The latter case might be expected when an anti-bonding electron is promoted to a non-bonding state.

Treatment of Data (1–6)

Energies of the Observed Transitions. Energies are usually given in terms of reciprocal wavelengths, or wave numbers ($1/\lambda$), in units of cm^{-1}. From Planck's equation

$$E = h\nu \qquad (3)$$

and the relation

$$\lambda\nu = c \qquad (4)$$

we have

$$E = hc(1/\lambda) \qquad (5)$$

The first step, then, is to take the reciprocals of the observed wavelengths for the P and R series of each isotope. The accuracy of the data justifies five significant figures.

A portion of the data obtained from the high resolution 2′-0″ spectrum is contained in Table 1. In practice there are usually about 20 usable lines in the 2′-0″ spectrum. From the low resolution $1' \leftarrow 0''$ band, only the average energy of the $(J' = 0 \leftarrow J'' = 0)$ transition is obtained.

Interatomic Distance. The rotational spacing constant B_v is defined as

$$B_v = \frac{h}{8\pi^2 I_v c} \qquad (6)$$

where $I_v = \mu r_v^2$; μ = reduced mass = $m_1m_2/(m_1 + m_2)$; r_v = interatomic distance in vibrational level v; h = Planck's constant, and c = speed of light. B_v varies slowly as a function of vibrational level. By using the tabulated data, it is possible to determine

[3] The value is c_{vacuum}; these spectra are measured in cells containing air where $c_{air} = c_{vacuum}n^{-1}$. The index of refraction n for air in the region of 1.8 microns is 1.00027 (*10*). However, this correction is approximately of the same magnitude as the experimental scatter and has been ignored.

Table 1. Some Observed Transitions in the 2′-0″ Spectrum.

Number	Transition $J'-J''$	$H^{35}Cl$		$H^{37}Cl$	
		λ (μ)	ν (cm^{-1})	λ (μ)	ν (cm^{-1})
R series					
3	4–3	1.7420 ± 0.001	5740.5 ± 3.4	1.7430 ± 0.001	5737.2 ± 3.4
2	3–2	1.7470	5724.1	1.7480	5720.8
1	2–1	1.7520	5707.8	1.7533	5703.3
0	1–0	1.7578	5688.9	1.7590	5685.0
P series					
1	0–1	1.7703	5648.8	1.7715	5644.9
2	1–2	1.7772	5626.8	1.7785	5622.7
3	2–3	1.7847	5603.2	1.7859	5599.4

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$B_{v=0}$ and $B_{v=2}$, and to extrapolate to obtain $B_{v=(-1/2)}$ (or B_e),[4] the value at the minimum of the potential energy curve of Figure 3.

The Jth rotational level term[5] is related to B_v by the equation

$$E_J/hc = F(J) = J(J+1)B_v \quad (7)$$

Figure 4 shows that for P and R components that terminate in the same J level in the upper vibrational state,

$$R(J-1) - P(J+1) = F''(J+1) - F''(J-1) = (J+1)(J+2)B_{v=0} - (J-1)(J)B_{v=0} \quad (8)$$

or

$$\Delta_2F''(J) = R(J-1) - P(J+1) = 4B_{v=0}(J+1/2) \quad (9)$$

Similarly, for P and R components starting from the same J level in the lower vibrational state,

$$\Delta_2F' = R(J) - P(J) = 4B_{v=2}(J+1/2) \quad (10)$$

Table 2 gives sample values calculated for $J = 0$ to $J = 3$ of $H^{35}Cl$. The values for $B_{v=0}$ and $B_{v=2}$ are obtained by summing and taking the average of the values of $\Delta_2F/4\ (J+1/2)$. In practice values for the transitions up to $J \cong 10$ for each series are obtained and used.

For an anharmonic oscillator, one in which the vibrational level spacings may be assumed to decrease linearly with v, B also is assumed to vary linearly according to the equation

$$B_v = B_e - \alpha(v+1/2) \quad (11)$$

By plotting B versus $(v+1/2)$ for $B_{v=2}$ and $B_{v=0}$ and graphically extrapolating to $v = -1/2$, the value B_e, the constant at the minimum of the potential energy curve of Figure 3, may be obtained. Using this, the value for the interatomic distance, r_e, may be determined. If desired, the value for α may be determined from the slope of the line. This series of calculations may be done for either isotope.

Vibration and Rotation Frequencies. It is possible to determine very precisely the energy of the (missing) $0'$-$0''$ transition, and thus the vibration frequencies for both isotopes. In Figure 2, the missing line is *not* equidistant between the $R(0)$ and $P(1)$ lines. The energy between the missing line and the $R(0)$ line for each isotope corresponds to the transition from $v'' = 0, J'' = 0$ to $v' = 2, J' = 1$ and has the energy

$$F(J) = B_{v=2}(J)(J+1) = 2B_{v=2} \quad (12)$$

Similarly, the energy from the $0'$-$0''$ line to the $P(1)$ line is

$$F(J) = 2B_{v=0} \quad (13)$$

Interpolation using the two B values permits the determination of the energy of the $(2' = 0'')$ transition, and thus the calculation of the vibrational frequency for the molecule in the $v = 2$ level. The corresponding transition on the low resolution $(1'$-$0'')$ spectrum is determined merely by inspection.

Using the two values of the $(2', 0' \leftarrow 0'', 0'')$ transition for $H^{35}Cl$ and $H^{37}Cl$, the experimental isotopic shift may be compared with that predicted from theory.

Since

$$\nu = (1/2\pi)\sqrt{k/\mu} \quad (14)$$

therefore

$$\frac{\nu(0-0, H^{35}Cl)}{\nu(0-0, H^{37}Cl)} = \left(\frac{\mu\ H^{37}Cl}{\mu\ H^{35}Cl}\right)^{1/2} \quad (15)$$

where the reduced masses must be calculated using extremely precise isotopic masses. If only low resolution instruments are available, the isotopic shift of DCl may be studied.

The frequency of rotation of the HCl molecule varies with the rotational level and to a smaller degree with the vibrational level. The frequency is given by the expression:

$$\nu_{rot}(J) = 2cB_v\sqrt{J(J+1)}\ (sec^{-1})$$

Anharmonicity. In the simplest approximation (harmonic oscillator) the potential energy of the molecule is assumed to vary as the square of the interatomic distance and the vibrational energy levels are equally spaced. In fact, as shown in Figure 3, the actual curve shows a systematic deviation from the parabola (dashed curve). The energy $G(v)$ of the vibrational levels with respect to the minimum of the curve is given by the power series

$$G(v) = \omega_e(v+1/2) - \omega_ex_e(v+1/2)^2 - \omega_ey_e(v+1/2)^3 - \ldots \quad (16)$$

where ω_ex_e and ω_ey_e are called the anharmonicity constants.

Since the missing lines of the $(2' \leftarrow 0'')$ and the $(1' \leftarrow 0'')$ spectra correspond to $G(v=2)$ and $G(v=1)$, ω_ex_e may be evaluated.

Taking

$$[G(v=1) - G(v=0)]$$

and

$$[G(v=2) - G(v=1)][= \Delta G]$$

gives the spacing between levels.

$$\Delta G = \omega_e - 2\omega_ex_e(v+1) \quad (17)$$

The difference $\Delta G(2\text{-}1) - \Delta G(1\text{-}0) = \Delta_2G$ gives the anharmonicity

$$\Delta_2G = -2\omega_ex_e \quad (18)$$

[4] The subscript e indicates an extrapolated value.

[5] The word *term* is used to signify energy expressed in reciprocal centimeters (cm^{-1}) instead of ergs or other units.

Table 2. Determination of the Rotational Constant B ($H^{35}Cl$).

J	$R(J)$ (cm^{-1})	$P(J)$ (cm^{-1})	$\Delta_2F''(J)$[a]	$B_{v=0}$	$\Delta_2F'(J)$[b]	$B_{v=2}$
0	5688.9 ± 3.4					
1	5707.8	5648.8 ± 3.4	62.1	10.350	59.0	9.832
2	5724.1	5626.8	104.6	10.460	97.3	9.731
3	5740.5	5603.2	145.3	10.379	137.3	9.807
			Average	10.396		9.790

[a] $\Delta_2F''(J) = R(J-1) - P(J+1)$ (Equation (9)).
[b] $\Delta_2F'(J) = R(J) - P(J)$ (Equation (10)).

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Dissociation Energy. Using the first anharmonicity constant, the dissociation energy of the molecule may be estimated crudely by means of the linear Birge-Sponer extrapolation (*2–4, 6*). Equation (17) indicates that the spacing between levels decreases with v and eventually reaches zero. Figure 3 shows that the dissociation energy $D_0°$ is the sum of the ΔG values up to $\Delta G = 0$. This summation may be made graphically and is the area under a plot of ΔG ($= \Delta\nu$) versus v. Figure 5 shows such a plot made using the two observed frequencies and the linear extrapolation. The dissociation energy is

$$D_0° = \omega_e^2/4\omega_e x_e - {}^1/_2\omega_e = \text{area} - {}^1/_2\omega_e \qquad (19)$$

Usually the second and higher anharmonicity terms $\omega_e y_e \ldots$ become important for large v and the curve drops more rapidly as shown by the dotted line. Thus linear extrapolation tends to an upper limit for $D_0°$ (*6*)

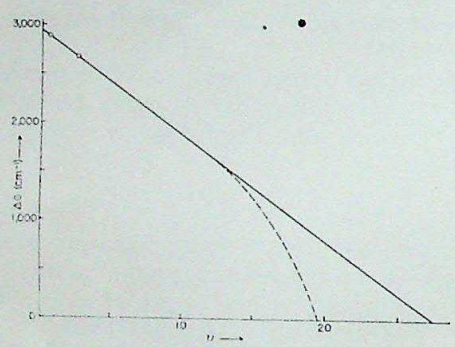


Figure 5. Linear Birge-Sponer extrapolation for HCl. The actual extrapolation (dashed line) is obtained if second and higher anharmonicity terms are used.

Rotational Temperature. Temperature may be defined as the parameter T in the Boltzmann equation

$$n_i = n_0 \frac{g_i}{g_0} e^{-\epsilon_i/kT} \qquad (20)$$

where the g's are statistical weights. For rotation, this becomes

$$n_i = n_0(2J + 1)e^{-J(J+1)Bhc/kT} \qquad (21)$$

where k is the Boltzmann constant and all the other parameters are known except T. Since, by Beer's law, $\log I/I_0$ is related to the number of molecules, the following expression may be derived.

$$\log \frac{(-\log I/I)_0}{(J' + J'' + 1)} = A - \frac{J''(J'' + 1)B''hc}{2.303\,kT} \qquad (22)$$

where A is a constant; the term in the left hand denominator takes into account that the absorption coefficient for the lines varies slightly with J. (The energy of the lower vibrational levels is used on the right hand side because this is an absorption spectrum.) The temperature then is inversely proportional to the slope of a plot of the left hand side versus $J''(J'' + 1)$. This means of measuring temperature is one of those used for high temperature arcs, jet engines, the sun and stars.

Isotopic Ratio. If the transition probability for any given line in the $H^{35}Cl$ spectrum is the same as for that in $H^{37}Cl$, the $^{35}Cl:{}^{37}Cl$ isotope ratio may be determined. Whether this assumption is valid should be tested by comparing the ratio of the logarithms of the intensities with accepted mass spectrographic data.

Results and Discussion

The calculated results are $B_{v=2,0,-1/2}$; α in eq. (11); and r_e for one or both of the isotopic molecules, as well as the isotope shift and average values of $\omega(v = 1,2)$, $\omega_e x_e$, $D_0°$ and T. Literature values for all of the molecular parameters are available (*6–8, 11–15*).

Table 3. Results ($H^{35}Cl$).

	Experimental[a]	Literature
$\omega_e x_e$	50.60	52.05[b]
B_e	10.550	10.5909[b]
α_e	0.302	0.3019[b]
r_e	1.285 Å	1.2746 Å[b]
$D_0°$	5.2854 ev[d]	4.430 ev[b]
$-\frac{G° - H_0°}{T}$ (298°K)	37.769 cal/deg	37.720[c]
$S°$ (298°K)	44.685 cal/deg	44.645 cal/deg[c]
$C°$ (298°K)	6.938 cal/deg	6.964 cal/deg[c]

[a] From a student report.
[b] Herzberg—appendix—Table 23, Ref. (*6*).
[c] JANAF Thermochemical Table, Ref. (*7*).
[d] Linear Birge-Sponer extrapolation.

The basic uncertainty in the wavelength data obtained with the Cary is $\pm 0.001\mu$ or $\pm 0.05\%$. When the differences in wave numbers are taken to obtain the $\Delta_2 F$, an average uncertainty of $\pm 2\%$ results. Since approximately ten sets of differences are averaged to obtain the interatomic distance, this expected uncertainty is reduced to approximately $\pm 1\%$. (Greater deviations from the literature value probably are due to remediable systematic error.) For the other quantities, greater uncertainties result from the way that differences are taken and from the higher uncertainty of the (1′-0″) data. In the calculation of T, it was assumed that B is constant with J. In fact, due to centrifugal stretching of the molecule, B decreases with increasing J. This introduces a slight systematic error.

Since about 20 lines are observed for each isotopic molecule, 20 data points are available. With these, the interatomic distance, the frequencies of rotation and vibration as well as the change of interatomic distance with change in vibrational level are calculated. The depth $D_0°$ of the potential energy curve also is estimated. Thus, this one experiment gives a fairly complete and detailed description of the molecule.

Thermodynamic Properties (*8*). Using the molecular description, the macroscopic thermodynamic properties may be predicted extremely accurately by means of statistical thermodynamics. The dissociation energy is simply $D_0°$. The free energy function (*9*) is given by

$$-\frac{G° - H_0°}{T} = R({}^3/_2 \ln M + {}^5/_2 \ln T) - 7.283 \text{ cal/deg} + R(-\ln y - \ln \sigma) - R \ln (1 - e^{-u})$$

The entropy S is

$$S° = R({}^3/_2 \ln M + {}^5/_2 \ln T) - 2.315 \text{ cal/deg} + R(1 - \ln y - \ln \sigma) + \left[R\frac{u}{e^u - 1} - \ln(1 - e^{-u})\right]$$

The specific heat $C°$ is

$$C° = {}^7/_2 R + R\frac{u^2 e^u}{(e^u - 1)^2}$$

where M = molecular weight, σ = symmetry number (1), $y = hcB/kT$, $u = h\omega c/kT = 1.438\omega/T$.

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Related Experiments. The molecule HBr also is suitable for this experiment, but the (1-0) band cannot be obtained using a quartz cell. Studies of the electronic spectra of iodine including the graphical Birge-Sponer extrapolation, and of atoms, also have been described (*16*, *17*).

Acknowledgment

The authors wish to thank Professor Paul Bender of the University of Wisconsin for making available a similar manuscript before its publication.

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Heat of Vaporization of I_2 Using Absolute Entropy Data

A physical chemistry experiment

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The purpose of this article is to present a student experiment using a powerful method of calculating enthalpy changes from equilibrium constant data. With this method, the experimental data are supplemented with entropy data obtained from the literature or calculated by statistical methods. Each experimental point yields a value of the enthalpy change, ΔH, *via* the relation $-RT \ln K = \Delta G = \Delta H - T\Delta S$. Iodine is chosen as the subject of the experiment because it might be studied in conjunction with the I_2 band spectrum experiment (*1*), because it is a relatively simple and well known system, and because the student himself may calculate all of the thermodynamic functions for I_2 (gas).

The classical method for reducing vapor pressure measurements to heat of vaporization ΔH is that of the "second law" or Clausius-Clapeyron equation

$$R d \ln K/d(1/T) = \Delta H_T \qquad (1)$$

where R is the gas constant, 1.9873 cal mole^{-1} deg^{-1}, and K is the equilibrium constant which for a vaporization process is equal to the vapor pressure, P. Use of this equation requires only measurements of relative pressure as a function of temperature. However, these measurements must be quite accurate and must cover a wide temperature-pressure range.

Alternatively, we have equation (2)

$$\Delta G^\circ_T = -RT \ln K = \Delta H^\circ_T - T\Delta S^\circ_T \qquad (2)$$

where the symbols have their usual meaning. Since K and T are measured directly, a knowledge of ΔS provides a means of obtaining ΔH from only one experimental point. The ΔS required may be calculated easily for solids or for simple gaseous species using either heat capacity or spectroscopic data and the third law of thermodynamics, hence the name, absolute entropy or *third law method*. In recent years the advantages of this method of calculation have become so widely appreciated that it is universally adopted in high temperature and many other fields of chemistry.

In the remainder of this report, the equations necessary for the "third law" calculations are developed, their applications are outlined and their salient features, including effects of experimental error discussed.

The Third Law Method Equations

Although ΔS was used in equation (2) for purposes of illustration, it is far more useful to use another function formulated by Giauque (*2*) and called the *free energy function, fef*.

[1] In the literature, either 298°K (meaning 298.15°K) or 0°K is used as the reference temperature. The first is more convenient if the *fef* are calculated from heat capacity data, the latter if calculated from spectroscopic data.

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$$fef = \frac{(G^\circ_T - H_{298})}{T} = -S^\circ_T + \frac{1}{T}\int_{298}^{T} C_p\, dT \quad (3)$$

where 298°K has been chosen as the temperature of reference.[1] The integral in equation (3) is equal to $(H^\circ_T - H_{298})$ so that *fef* is identical with S except for a term involving heat capacity.

Use of the *fef* instead of entropy leads to some of the main advantages of the third law calculation and has been discussed by Margrave (*3*, *4*). In summary, these advantages are

1. *fef* is easier to calculate from spectroscopic data.
2. *fef*, and to a greater extent Δfef, varies very slowly with temperature and may be tabulated at wide temperature intervals; the reason for this is given in the discussion of equations (5);
3. Because of the heat capacity term in equation (3), reduction of data using *fef* gives directly ΔH at 298°K. When the values from each experimental point are compared with one another, any systematic variation of ΔH_{298} with temperature of measurement is indicative of systematic errors. Such a clear cut indicator does not occur in the "second law" method.

Equations (2) and (3) may be combined to give the equation used for the reduction of the vapor pressure data:

$$\frac{\Delta H_{T'}}{T} = -R \ln P\,(\text{atm}) - \left[\frac{G^\circ_T - H^\circ_{T'}}{T}(\text{vap}) - \frac{G^\circ_T - H_{T'}}{T}(\text{condensed})\right] \quad (4)$$

where T is the temperature at which the measurement is made; T' is the reference temperature, 298°K; R is the gas constant, 1.9873 cal mole^{-1}deg^{-1}; and the quantity in brackets the change in free energy function. It may be verified that equation (4) is an identity.

The Free Energy Function

The values of *fef* are obtained from the valuable compilation of Stull and Sinke (*5*). This gives $(G^\circ_T - H_{298})/T$ for I_2(solid) at 300°K = −27.90 cal deg^{-1} mole^{-1}, and for I_2 (gas), −62.34. The change in free energy function for vaporization is, therefore, −34.44 cal deg^{-1}mole^{-1}. Since *fef* changes very slowly with temperature, this value may be used for all of the calculations connected with this experiment.

The value of free energy function for the condensed phase is obtained from precise measurements of heat capacity (*6*). However, those for the gaseous molecule are obtained from spectroscopic data by statistical calculations:

As with entropy,

$$(G^\circ_T - H_0^\circ)/T = fef = fef\,(\text{translation}) + fef\,(\text{vibration}) + fef\,(\text{rotation}) + fef\,(\text{electronic}) \quad (5)$$

The necessary formula for each of these terms are developed in "Thermodynamics" or "Quantum Chemistry" texts (*7*, *8*) and are summarized below

$$\begin{aligned} -fef\,(\text{trans}) &= R(3/2 \ln M + 5/2 \ln T) - 7.283 \text{ cal/deg} \\ -fef\,(\text{rot}) &= R(\ln T + \ln \mu + 2 \ln r - \ln \sigma) - 6.335 \\ -fef\,(\text{vib}) &= -R \ln [1 - \exp(-hc\omega/kT)] \\ -fef\,(\text{elec}) &= R \ln (\text{statistical weight})\ (=R \ln 1 = 0) \end{aligned} \quad (5)$$

where atomic mass units are to be used for molecular weight and reduced mass, and angstroms for interatomic distance r. The necessary information for I_2 is tabulated in Table 1 and has been obtained from the compilation of Herzberg (*9*).

Table 1. Parameters for the Calculation of the Free Energy Function of $I_2(g)$

M	Molecular weight (atomic mass units)	253.8 amu.
μ	Reduced mass (atomic mass units)	63.45 amu.
r	Interatomic distance	2.67 Å
σ	Symmetry number	2
	Vibration frequency	215 cm^{-1}
	Statistical weight of low lying electronic states	1
hc/k		1.4388 deg-cm
2.303 R		4.5758 cal deg^{-1}

The equations (5) are not sensitive to uncertainties in the molecular parameters r and ω which are least well known. Only the logarithms of the vibration frequency and interatomic distance enter into the *fef* and they are overshadowed by the large additive terms in ln M and ln T. The main variation of *fef* (total) with temperature is due to a 7/2 ln T term. Thus *fef*, and especially Δfef, should vary very slowly with temperature.

These calculations give *fef* with a 0°K reference. To compare them with the values for $I_2(g)$ given previously, one uses the correction $(H_{298} - H_0) = 2.418$ cal/mole, which also comes from spectroscopic data.

The student is asked to calculate the *fef* for the gas in order that he see the relative magnitudes of the vibrational, rotational and translational contributions, and also the ease of calculation. He is asked also to compute the error introduced into the total *fef* if either vibrational frequency ω, or interatomic distance r were in error by ±20%. (20% would be a large uncertainty for a diatomic molecule.)

The Experiment

Measurements are made equally well with a recording spectrophotometer or with a manual instrument such as the Beckman DU. Some iodine crystals are placed in a 10 cm absorption cell and allowed to come to equilibrium. The absorption at 5200 Å, averaged over several bands or taken with a very wide slit, is measured following the instrument manufacturer's instructions and the temperature is recorded to 0.1°C. When a thermostatted cell holder is available, several readings should be made covering the range 20 to 45°C, preferably at 4–6° intervals. Temperatures first are increased systematically, then decreased. A blank is necessary to determine the zero line.

If a thermostatted cell holder is *not* available, one measurement is taken and will be sufficient to give a ΔH.

Treatment of Data

Absorption measurements may be converted to pressures using Beer's law

$$\text{Optical Density} \equiv -\log I/I_0 = L\alpha n \quad (6)$$

where L is the path length of the cell in centimeters, α the absorption coefficient in units of liters moles^{-1}

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cm^{-1}, and n the number of moles of absorbing material per liter. For I_2 at 310°K, and 5200 Å, α = 7.3×10^2 liters $mole^{-1}cm^{-1}$ (decimal logarithms) (*10*).

The vapor pressure of I_2 is then

$$P = nR'T = -R'T\frac{\log (I/I_0)}{L\alpha} \qquad (7)$$

where R' is 0.082 l-atm deg^{-1}-$mole^{-1}$.

The value of P from equation (7) may be substituted directly into equation (4) and the ΔH computed. As Δfef does not change rapidly with temperature, the value for 300°K suffices for all calculations.

Results

The values of ΔH_{298} obtained are tabulated in the sequence of measurement corresponding to the systematic variation of temperature. Use of *fef* (solid) from (5) rather than the slightly more accurate ones of (6) means that the ΔH_{298} should be compared with that of (5). The vapor pressures obtained still should be accurate and may be compared with the original data of Baxter, Hickey, and Holmes (*6a*).

Table 2 gives data and results abstracted from a more complete student report. The data were taken first with rising then falling temperature such that temperature gradients would be expected. This is reflected clearly in both the trend of the ΔH_{298} and the shift in values. The log P versus $1/T$ plots (15 points) showed distinct lines for rising and falling T with slopes equivalent to 10.0 and 9.5 kcal/mole, respectively.

It is informative to compare the third law calculation with the second law calculation. Even in the present case with highly exaggerated thermal gradients, the third law calculation gives a good answer, although the very close agreement with the literature is fortuitous. Also, the method permits ΔH to be obtained from a single experimental measurement. This is not obtained *gratis* but is "bought" with *fef* data, when such are available to replace additional pressure-temperature measurements. Experimental errors in pressure are less significant than in the second law calculation. Assuming that second law data were taken over a range of 30°, a 3° error in ΔT would produce a 10% error in ΔH. If the pressure range were 10^2, an error of 10% in the highest pressure compared to the lowest would produce 2% error in the heat, or about 0.300 kcal/mole. In the third law treatment, a 3° error at 300° K gives a discrepancy of 1% in ΔH; 10% in the pressure at the same temperature gives 0.056 kcal/mole. An example of an error calculation for third law treatment of data for hitherto unknown molecules is given in (*11*).

Table 2. Computation of $\Delta H°_{298}$ (vap)[a]

T (°K)	Log I_0/I	Log P (mm)	$\Delta H°_{298}$ kcal/mole
303.5	0.175	−0.344	14.90
311.8	0.260	−0.176	15.05
318.0	0.380	+0.014	15.09
314.7	0.430	+0.063	14.82
309.4	0.360	−0.022	14.75
301.5	0.230	−0.228	14.64
		Average	14.9 ± 1.5
		Literature (*5*)	14.88

[a] Temperature gradients were present when the data were taken.

Conclusion

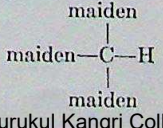
The heat of vaporization of I_2 has been calculated from experimental absolute vapor pressure data and literature values of free energy functions. This calculation may be compared to the usual "second law" or Clausius-Clapeyron calculation which requires relative vapor pressure data over a wide range of pressures. The two methods complement each other. However, when *fef* data are available or may be estimated, the third law calculation gives results that are relatively insensitive to errors in the pressure-temperature measurements and that provide a "built in" indication of systematic errors.

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Chem Gem

A contribution to the advertising men from an elementary organic chemistry class sent in by Gene Zeigler, Illinois Institute of Technology: the formula for *Maidenform*.



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The Dissociation Quotient of Bromcresol Green

A class study of ionic strength effects

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A few years ago I proposed an experiment on the solubility of calcium sulfate as a function of ionic strength (*1*), one major purpose of which was to allow the student to use his own analytical data to learn something about activity coefficients. It still seems naive to try to teach equilibrium theory without a good treatment of the activity concept, and the present paper deals with a more sophisticated experiment which has involved the cooperation of the entire class. The purposes of this study include the use of spectrophotometry, a thorough application of various acid-base equilibrium principles, and a realistic look at the behavior of activity coefficients.

Bromcresol green has been chosen as the acid-base system for the study for three reasons: it behaves as a simple monoprotic acid, apparently with no complications such as low solubility, dimerization, decomposition; the two members of the conjugate pair show greatly differing absorption spectra and even a simple filter photometer is excellent for the measurements; the dissociation quotient is in the same range as that of acetic acid, thus making the easy-to-handle acetate-acetic acid buffer system eminently suited for *p*H control. Methyl red could also serve well for this experiment, and indeed has been proposed for student work in determining dissociation quotients (*2*), but it has the disadvantage of being a diprotic acid with fairly close dissociation constants (*3*).

If we regard the acid form of bromcresol green as

$$\underset{\text{yellow}}{HB^-} + H_2O \leftrightharpoons \underset{\text{blue}}{B^=} + H_3O^+$$

simply HB^-, then and in terms of activities:

$$K = \frac{a_{H_3O^+} \cdot a_{B^=}}{a_{HB^-}} \qquad (1)$$

If the symbol Q is used to represent the dissociation quotient in terms of molarities at equilibrium, then

$$K = Q \cdot f \quad or \quad pQ = pK + \log f \qquad (2)$$

where f is really a ratio of activity coefficients. However, at low ionic strength according to the Debye-Hückel theory the activity coefficients of H_3O^+ and HB^- should approximately cancel because both are singly-charged ions, although there would be some difference because of ionic size considerations. Then, if f is taken to represent only the activity coefficient of the doubly-charged $B^=$ ion the Debye-Hückel equation would predict (taking 7 Å as the diameter of the ion (*4*)):

$$\log f = -\frac{2.04\mu^{1/2}}{1 + 2.3\mu^{1/2}} \text{ at } 25°C \qquad (3)$$

Therefore, it would be expected that a plot of experimental values of pQ versus corresponding values of the quantity $\mu^{1/2}/(1 + 2.3\mu^{1/2})$, hereafter referred to as μ' for simplicity, should be linear with a slope of -2.04 and an extrapolated intercept equal to the thermodynamic value of the dissociation constant, pK. As the ionic strength increases equation (3) becomes less and less accurate, and usually gives log f values which are increasingly too negative. Therefore equation (3) is often supplemented with an empirical term, $+ C\mu$, where the value of C depends on the system under study. In this experiment the instructor may choose to deal with this constant by asking the students to attempt its evaluation after the class results are in.

Laboratory Directions. Into a 100-ml volumetric flask pipet 10 ml of 3×10^{-4} *M* bromcresol green solution and 5 ml of 0.200 *M* sodium acetate solution. Use a siphon buret to add the quantity of 1.00 *M* potassium chloride which is assigned on an individual basis, such that the maximum ionic strength to be used is 0.50. (Of course, the instructor can set any arbitrary maximum depending on how much interest he wishes to attach to deviations from the Debye-Hückel predictions). Dilute to the mark with distilled water, mix, and pour "quantitatively" into a 250-ml beaker.

Clean the volumetric flask, pipet 25 ml of 1.00 *M* acetic acid, and again use the siphon buret to add not only the assigned amount of potassium chloride but also an additional amount to make the ionic strength of the resulting solution the same as that of the sodium acetate solution. Dilute, and mix.

Use the filter photometer to determine the absorption spectrum of the sodium acetate solution of bromcresol green, taking care to make a precise measurement at the wavelength where there is maximum absorption. Pour the sample back into the beaker, being careful not to lose any because the volumes must be known for the calculations. Add precisely 2.00 ml (from pipet or buret) of the acetic acid solution. Mix well with a stirring rod, and measure the absorbance at the wavelength of maximum absorption of the blue form of the dye. Repeat this procedure for additional 2.00-ml increments of acetic acid, and (for the record) determine the absorption spectrum in the case of the buffer which is equimolar in acetate and acetic acid. After five such measurements have been made, add 1.0 ml of 3 *M* hydrochloric acid and again measure the entire spectrum.

Correct all absorbance readings for the effect of dilution by multiplying each observed value by the factor $(100 + v)/100$, where v is the volume of acetic acid (and hydrochloric acid) added. Plot the three absorption spectra on a single sheet of graph paper.

Calculate the five values of the bromcresol green dissociation quotient, being careful to use the proper value of the acetic acid dissociation quotient for your particular ionic strength (see below). Show the five values, and their average, in a table including Q, pQ, buffer *p*H, and corrected absorbance. Calculate the values of μ and μ' for your solutions, enter the values along with your average pQ in the table on the bulletin board, and also place a map tack representing your results on the large graph of pQ versus μ'. After most of the class results are posted, choose about ten values which seem to be representative of the set, spread over the entire range of μ', and make a graph for your notebook. Evaluate the thermodynamic value, pK, by drawing a line having the theoretical Debye-Hückel slope through the points of lower ionic strength.

In your notebook comment on the agreement, or lack thereof, between the class results and the Debye-Hückel predictions. By considering a few of the points deviating at higher ionic strength,

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estimate a value for the Hückel extension constant, C. Suggest ways in which the experiment might be improved.

Calculation of pH Values

From the definition of Q, it is necessary to know the $[H_3O^+]$ of each buffer solution used in the absorbance measurements. Although it would be possible to use a pH meter for an approximate determination, in this experiment it is more accurate to calculate the pH because the dissociation quotient of acetic acid is accurately known (*5*) in a variety of electrolyte solutions. For convenience, Table 1 lists the values for a

Table 1. Dissociation Quotient of Acetic Acid in KCl at 25°C

M KCl:	0.00	0.02	0.03	0.06	0.11
$Q \cdot 10^5$:	1.754	2.302	2.415	2.650	2.891
M KCl:	0.21	0.51	1.01	2.01	
$Q \cdot 10^5$:	3.151	3.340	3.071	2.182	

series of potassium chloride solutions at 25°C. The instructor should provide a carefully-made graph of these values, so that each student can read off the appropriate value for his particular ionic strength. Two graphs are best: one for the entire range, and one with an expanded scale for the lower ionic strength range only. In this way the student can obtain a reliable value for Q_{HOAc}.

Since the quantities of sodium acetate and acetic acid have all been measured precisely, a reliable set of values for $[H_3O^+]$ is easily calculated:

$$(H_3O^+) = Q_{HOAc} \cdot \frac{[HOAc]}{[OAc^-]} = Q_{HOAc} \cdot \frac{0.25v}{1} \qquad (4)$$

where the acetic acid : acetate ratio is expressed in terms of millimoles.

Interpretation of the Spectrophotometric Data

It has already been mentioned that the absorbance values should be corrected for the effect of dilution. In the initial sodium acetate solution the pH is high enough (students should prove this) that the bromcresol green is virtually entirely in the blue form, and the absorbance is symbolized by A_B. At the end of the experiment, when the hydrochloric acid has been added, the pH is low enough (prove this also) to insure "complete" conversion to the yellow form, and the final (corrected) absorbance is A_{HB}. The five intermediate solutions are a series of acetate-acetic acid buffers, the pH values such that a mixture of the blue and yellow forms are present, and if the absorbance is designated as A for a given solution, then it can be shown that the ratio of blue to yellow form in that buffer is given by:

$$\frac{[B^-]}{[HB^-]} = \frac{A - A_{HB}}{A_B - A} \qquad (5)$$

Thus, the results of equations (4) and (5) can be combined for the calculation of the bromcresol green dissociation quotient for each of the five solutions.

Typical Student Results

Figure 1 shows the absorption spectra of bromcresol green as obtained by a student in the course of this experiment, using a Leitz-Ruoy photometer. The points corresponding to the 10 filter choices have been connected with straight line segments to emphasize that the filter instrument does not allow the precise shape of the curves to be determined.

Table 2 shows the calculated results obtained in this case. It can be judged from the precision of agreement among the Q values that the simple photometer is quite adequate for the task. Figure 2 shows a few typical results from the range of ionic strength used. It is seen that the line with the theoretical slope fits nicely the points at lower ionic strength (a μ' value of 0.215 corresponds to an ionic strength of 0.18), in spite of the

Table 2. Student Results for Bromcresol Green Study (Data of Oren Anderson)

v (of HOAc)	A	buffer pH	$Q \cdot 10^5$	pQ
0	0.721	basic	...	...
2.00	0.465	4.983	1.88	4.726
4.00	0.342	4.682	1.86	4.730
6.00	0.272	4.506	1.86	4.730
8.00	0.225	4.381	1.85	4.732
10.00	0.191	4.284	1.84	4.736
+ HCl	0.002	acidic	average Pq:	4.731

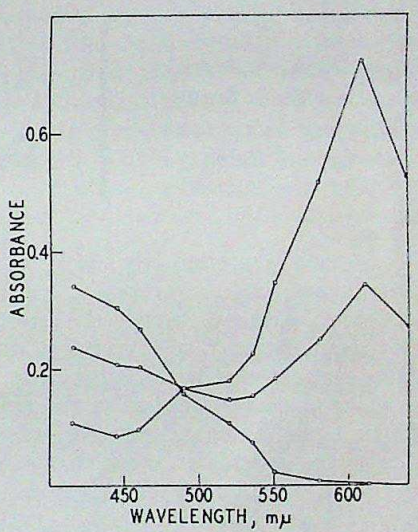


Figure 1. Absorption spectra of bromcresol green as determined with a filter photometer. Upper curve: sodium acetate solution. Middle curve: equimolar acetic acid, sodium acetate buffer. Lower curve: after addition of slight excess of hydrochloric acid. Absorbances corrected for dilution. Data of Oren Anderson.

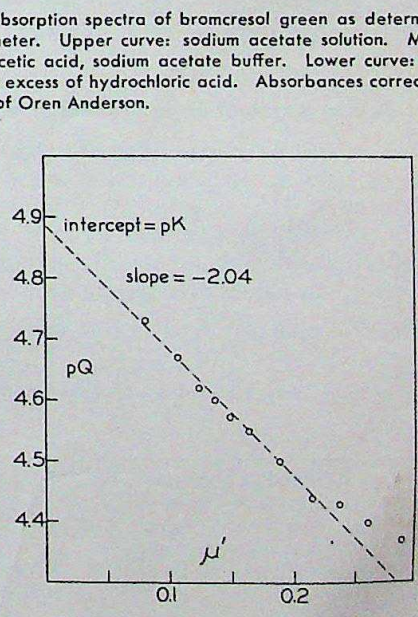


Figure 2. Typical class results in the determination of pK for bromcresol green. See text for definition of μ'.

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fact that no effort was made to control temperature effects. The extrapolated intercept of $pK = 4.89$ is in excellent agreement with the literature values for bromcresol green (*6–8*).

In conclusion, this experiment has worked exceptionally well in student hands, and since the actual laboratory work may be done rather quickly, it is not necessary to have a large number of filter photometers available. By the time the student has carried out the calculations, he has learned not only some spectrophotometric principles, but also has had a pretty thorough workout on a variety of acid-base calculations. The cooperation of the class leads to a better understanding of the effects of ionic strength, and shows both the value and limitations of the Debye-Hückel equation.

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Random and Systematic Errors in the Determination of Association Constants

During a preliminary study of association equilibria in solution of carboxylic acids and of amides, carried out with an improved version of the thermoelectric osmometer[2,3] of Brady *et al.*,[4,5] the authors became concerned with the large magnification factors connecting the uncertainties in the experimental data with that of the derived equilibrium constant, and with the large systematic error in the constant produced by even a small vapor pressure of any participating species. Since these effects have neither been considered nor discussed thoroughly in the literature, a short presentation of the arguments appears appropriate.

Uncertainty Due to Random Experimental Errors

The discussion will be restricted to the dimerization

$$2N_1 \rightleftarrows N_2$$

and Raoult's law will be assumed to hold for each species (similar considerations would apply to more complex cases). The experimental data are:

$N = N_1 + 2N_2$; the total mole fraction expressed in terms of monomer

$\bar{N} = \dfrac{-\Delta p}{p_0}$; measured "osmotic" total mole fraction at equilibrium

For solute species with negligible vapor pressure $\bar{N} = N_1 + N_2$, and the equilibrium constant is given by:

$$K = \frac{(N_2)}{(N_1)^2} = \frac{(N - \bar{N})}{(2\bar{N} - N)^2} \tag{1}$$

Differentiation, introduction of $X = \bar{N}/N$, and algebraic manipulation leads to

$$\frac{\delta K}{K} = \frac{\delta N}{N}\left[\frac{1}{(1-X)(2X-1)}\right] + \frac{\delta \bar{N}}{N}\left[\frac{3-2X}{X}\cdot\frac{1}{(1-X)(2X-1)}\right] \tag{2}$$

the absolute values of the differentials being taken since the errors in N and $\bar{N}$ are independent.

In Table 1, columns 2 and 3, the factors by which the relative uncertainties $\delta N/N$ and $\delta\bar{N}/N$ in the measurements are multiplied to give the relative uncertainty in K are shown as functions of X. Even at $X = 0.8$, at about the minimum value of the factors, an experimental uncertainty of $^1/_2\%$ each in N and $\bar{N}$ leads to a maximum uncertainty in K of about 11% and a standard uncertainty of 8.3%, for a single determination.

Table 1

X	$\dfrac{1}{(1-X)(2X-1)}$	$\dfrac{3-2X}{X}\cdot\dfrac{1}{(1-X)(2X-1)}$	$\dfrac{3-2X}{1-X}$
0.95	22.2	25.8	22
0.90	12.5	16.7	12
0.85	9.5	14.5	8.7
0.80	8.3	14.5	7
0.75	8.0	16.0	6
0.70	8.3	20.0	5.3
0.65	9.5	24.9	4.9
0.60	12.5	37.5	4.5
0.55	22.2	76.7	4.2

[1] The authors are indebted to Mechrolab, Inc., Mountain View, California for partial support of this work.
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[5] The present instrument has been described at the "Thirteenth Annual Conference on Electrical Techniques in Medicine and Biology" Bethesda, Maryland, October, 1960.

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For $X = 0.55$, equivalent to a degree of association of 0.9, which is not unusual for such studies, the same experimental uncertainty represent a standard uncertainty of about 40% in K.

Systematic Error Due to Volatility of Solute

Some of the major methods for determining the activity of the solvent in a solution, i.e., the ebullioscopic, isopiestic, and thermoelectric methods, are based on the direct or indirect measurement of total vapor pressure over the solution relative to the pure solvent or to a solution of known vapor pressure. It is in general assumed that the solutes have no vapor pressure of their own; however, a solute with even a small partial pressure introduces a quite significant systematic error.

If each solute species, mole fraction N_i, has in its pure state a vapor pressure p_i, then

$$p = (1 - \sum_i N_i)p_0 + \sum_i N_i p_i \qquad (3)$$

In the case of dimerization, it might reasonably be assumed that the vapor pressure of the dimer can be neglected; this is, however, not necessarily so for the monomer. In this case, equation (3) can be rearranged to give the apparent "osomotic" mole fraction

$$\bar{N} = -\frac{\Delta p}{p_0} = N_2 + N_1(1 - \Delta) \qquad (3a)$$

where $\Delta = p_1/p_0$. The true equilibrium constant is

$$K = \frac{[1 - 2\Delta][N(1 - \Delta) - \bar{N}]}{(2N - \bar{N})^2} \qquad (4)$$

and, if K' is the constant calculated from equation (1) which neglects Δ,

$$\frac{K}{K'} = \left(1 - \frac{\Delta}{1 - N}\right)(1 - 2\Delta) \approx 1 - \Delta\left(\frac{3 - 2N}{1 - N}\right) \qquad (5)$$

In the last column of Table 1 the factor $(3 - 2X)/(1 - X)$ is given as a function of X. Its value is quite large, especially at low degrees of association, and even at virtually complete association it has a limiting value of four.

For the calculation of the actual error it remains to estimate Δ. The value of Δ for any solute can be estimated in first approximation from its boiling point by assuming Trouton's rule (taking the entropy of vaporization at the boiling point as 21 cal $(°K)^{-1}$) and using the Clausius-Clapeyron equation

$$\log_{10}\frac{P_0}{p_1} = 4.6\,\frac{T - T_0}{T} \qquad (6)$$

where T_0 and T_1 are the boiling points of solvent and solute and T is the temperature of measurement. In estimating T, it should be borne in mind that in the present case it refers to a hypothetical pure monomer. It appears justified to assign to such a monomer a boiling point about that of a structurally similar compound of the same molecular weight, which, however, is not able to polymerize.

For example, in the case of the extensively investigated benzoic acid association,[6] an appropriate monomer would be phenyl formate, bp 446°K. In Table 2 the values of Δ, using equation (6) and assuming benzene as a solvent, are given for different temperatures. Combining these results with those shown in the last column of Table 1, it is seen that significant

Table 2

t°C	20	40	60	80
Δ	0.035	0.043	0.052	0.061

systematic errors occur in the experimental constant, the magnitude of which depends pronouncedly on the degree of association and on temperature. At the boiling point of benzene, and for a degree of association of 0.5 ($X = 0.75$), the error amounts to over 30%. It is likely that these effects have not been detected because the large association constant of benzoic acid requires studying system at relatively high degrees of association where the systematic errors do not change rapidly with concentration. It is also obvious from equation (3) that even for quite significant values of Δ the partial pressure of a volatile solute at low concentration is very small, and that therefore transfer of solute through the vapor phase is undoubtedly extremely slow.

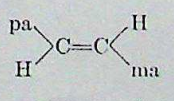
To arrive at the above estimate of errors caused by the partial pressure of the monomer, a number of assumptions were necessary. However, in principle both the true equilibrium constant K and Δ can be derived directly from precise experimental data for N and $\bar{N}$ obtained over a wide range of X. The only necessary condition is that the partial pressure of the monomer obey Henry's law. Equation (4) can be rewritten in the form

$$\frac{\bar{N}}{N}(=X) = (1 - \Delta) - \frac{K}{1 - 2\Delta}\,\frac{(2\bar{N} - N)^2}{N} \qquad (6)$$

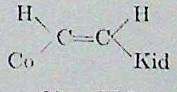
A plot of the experiment $\bar{N}/N$ versus $(2\bar{N} - N)^2/N$ would be a straight line with an intercept of $(1 - \Delta)$ and a slope of $-K/(1 - 2\Delta)$.

[6] See for example: Allen, G., and Caldin, E. F., *Trans. Faraday Soc.*, 49, 895 (1953); and Wall, I. T., and Banes, F. W., *J. Am. Chem. Soc.*, 67, 898 (1945).

Chem Gems



transparent



Cisco Kid

Gene Zeigler
Illinois Institute of Technology, Chicago, Illinois

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Contour Surfaces for Atomic and Molecular Orbitals

Models of atoms which show electrons moving in well defined orbits around the nucleus are not consistent with a vast body of experimental evidence or with current theories of atomic structure. The wave mechanical description of the electron in an atom arose from de Broglie's (*1*) wave theory of matter, and is contained in a wave equation proposed by Schrödinger (*2*) in 1926 (the symbols are defined in (*5*)):

$$\nabla^2\psi + \frac{8\pi^2\mu}{h^2}(E - V)\psi = 0$$

The equation describes a standing wave, and if some physical picture of the electron is to be retained an interpretation of ψ (wave function) in terms of some property of the electron is essential.

Since in Maxwell's wave theory of light ψ^2 was successfully related to the intensity of a light beam, Schrödinger (*2*) initially suggested that ψ^2 for an electron was a measure of its density at any point. A few months later, Max Born (*3*) gave the presently accepted interpretation of ψ. In view of the Heisenberg uncertainty principle (*4*), Born identified ψ^2 (or $\psi^*\psi$, i.e., the wave function times its complex conjugate when ψ contains imaginary parts) with the probability of finding the electron at that point. It is interesting to notice that the concept of a moving electron nowhere enters the description given by the Schrödinger equation, and in fact it is not possible to conceive of any classical motion that would result in most of the probability distributions that arise. Nevertheless, because the probability function ($\psi^*\psi$) is not time dependent, models of the atom in various stationary states can be constructed.

The ideal model of an atomic or molecular orbital would be a cloud-like structure showing the probability of finding an electron at all points in space relative to the nucleus. Although it is conceivable that a model could be made with a colored suspension in a clear plastic, the difficulty of preparing such a model precludes its use. Somewhat less effective, but more easily constructed models can be fashioned from styrofoam to represent contour surfaces. The surface visible must then represent a contour surface of constant ψ (wave function) or of constant $\psi^*\psi$ (probability function). There are a number of ways in which the surface could be labeled, e.g., (*a*) by the value of ψ relative to ψ_{max}, (*b*) by the value of $\psi^*\psi$ compared with $\psi^*\psi_{max}$, (*c*) by the fraction of $\psi^*\psi$ enclosed by the contour surface.

The last method is probably the most effective for labeling the surface since it gives the probability of finding the electron within the surface, or, as a less correct alternative, the fraction of the electron(s) enclosed by the contour surface. For purposes of computation it is more convenient to use method (*b*). We will now present a method by which contour surfaces can be calculated, and show how these can be used to construct some models that are useful for introductory courses in atomic and molecular structure.

Atomic Orbital Contour Surfaces

Cohen (*4*) has shown that these contours for a p orbital can be found by expressing the wave function in Cartesian coordinates and separating the variables. This cannot be done in general; hence it is appropriate to use polar coordinates in which the variables are always separable. The function $\psi^*\psi$ is given in Table 1 for a number of atomic orbitals. Strictly, these are correct only for "one electron" atoms, but are extended to the general case of a many electron atom by using an effective nuclear charge, Z, for a particular orbital (*6*). Though the effective nuclear charge varies with r we shall use an average value to make the calculations less formidable:

The method of obtaining contours will be developed in detail for the 3*d* orbitals of Ti(III), which has $Z \approx 9.2$. We consider first a $3d_{x^2-y^2}$ orbital, the contours of which are identical with those of the $3d_{xy}$, $3d_{xz}$ and $3d_{yz}$ orbitals except for their direction in the coordinate system. The electron density, $\psi^*\psi$, along the x axis, shown in Figure 1, is calculated from the appropriate function of Table 1 with $\theta = 90°$ and $\phi = 0°$. The contours of constant electron density are different in the xy and xz planes, and must be evaluated separately.

In the xy plane, we have, with $\theta = 90°$:

$$(\psi^*\psi)_{xy} = \frac{1}{3^8 2\pi}\left(\frac{Z}{a}\right)^3 \sigma^4 e^{-(2\sigma/3)} \cos^2 2\phi$$

in which a is the Bohr radius (0.529 Å), and $\sigma = Zr/a$. It is convenient to assume values of σ and calculate values of ϕ which give a chosen value of $\psi^*\psi$. This has been done for $\psi^*\psi$ equal to 0.316 and 0.10 of the maximum $\psi^*\psi$, with the results given in Figure 2. The same result can be found by a graphical solution

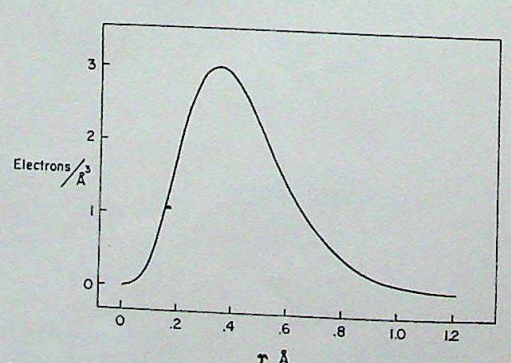


Figure 1. Electron density in a Ti(III) $3d_{x^2-y^2}$ orbital along the x (or y) axis.

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employing the curve of Figure 1 (Arya Samaj Foundation Chennai and eGangotri) 0) are found at values of ϕ that make $\cos^2 2\phi$ equal to zero ($\phi = 45°$, etc.).

The same procedure in the xz plane ($\phi = 0$) develops solutions of

$$(\psi^*\psi)_{xz} = \frac{1}{3^8 2\pi}\left(\frac{Z}{a}\right)^3 \sigma^4 e^{-2\sigma/3} \sin^4\theta$$

with the results shown in Figure 3. Thus the contour surfaces of the $d_{x^2-y^2}$ orbital are oval in cross section (see models in Fig. 11).

The $3dz^2$ orbital is independent of ϕ (see Table 1) hence the contour surfaces have cylindrical symmetry about the z axis. The electron density distribution is identical with that of Figure 1, except that the magnitude of the density is larger by a factor $^4/_3$. The contours are given in Figure 4 for the same fractions of the maximum electron density as above, although for the "doughnut" in the xy plane, the electron density does not reach 0.316 of the maximum. Nodes are found at $\theta = \cos^{-1}(1/3)^{1/2} = \pm 55°$.

A similar treatment for the $3p_z$ orbital of the chlorine atom ($Z \approx 6.1$) gives the electron density (along the z axis) shown in Figure 5 and the contour lines in Figure 6. The contour surfaces can be generated by rotation of this curve around the z axis. Aside from a node in the xy plane there is also a spherical node of radius $\sigma = 6$ or $r = 0.52$ Å. Similar curves are shown in Figures 7 and 8 for the $2p_z$ orbital of a carbon atom, previously treated by Cohen (*4*).

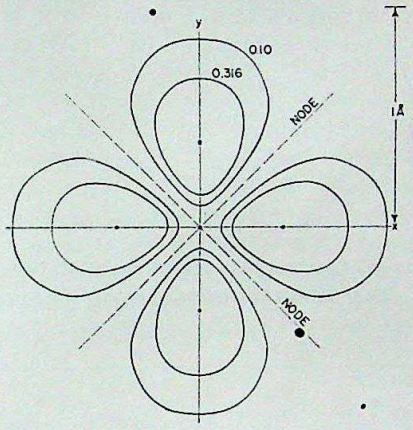


Figure 2. Contours of constant ψ^2 at 0.10 and 0.316 of maximum for a Ti(III) $3d_{x^2-y^2}$ orbital in the xy plane. There are two nodal planes perpendicular to the paper and bisecting the axis.

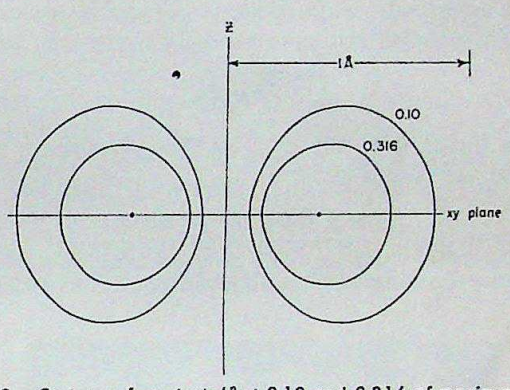


Figure 3. Contours of constant ψ^2 at 0.10 and 0.316 of maximum for a Ti(III) $3dz^2{-}y^2$ orbital in the xz plane. The z-axis is the intersection of the two nodal planes shown in Figure 2.

Table 1. Probability Functions for Hydrogen-Like Atoms

n	l	m	Orbital	$\psi^*\psi$
1	0	0	$1s$	$\frac{1}{\pi}(z/a)^3 e^{-\sigma}$
2	0	0	$2s$	$1/(2^5\pi)(z/a)^3(2-\sigma^2)e^{-\sigma}$
	1	0	$2p_0$	$1/(2^5\pi)(z/a)^3\sigma^2 e^{-\sigma}\begin{cases}\cos^2\theta\\ \sin^2\theta\\ \sin^2\theta\end{cases}$
		+1	$2p_{+1}$	
		−1	$2p_{-1}$	
3	0	0	$3s$	$1/(39\pi)(z/a)^3(27-18\sigma+2\sigma^2)^2 e^{-(2\sigma/3)}$
	1	0	$3p_0$	$2/(3^8\pi)(3/a)^3(6-\sigma)^2\sigma^2 e^{-(2\sigma/3)}\begin{cases}\cos^2\theta\\ \sin^2\theta\\ \sin^2\theta\end{cases}$
		+1	$3p_{+1}$	
		−1	$3p_{-1}$	
	2	0	$3d_0$	$\frac{1}{(2)3^8\pi}(z/a)^3\sigma^4 e^{-(2\sigma/3)}\begin{cases}{}^1/_3(3\cos^2\theta-1)^2\\ 4\sin^2\theta\cos^2\theta\\ 4\sin^2\theta\cos^2\theta\\ \sin^4\theta\\ \sin^4\theta\end{cases}$
		+1	$3d_{+1}$	
		−1	$3d_{-1}$	
		+2	$3d_{+2}$	
		−2	$3d_{-2}$	

An Alternative Orthogonal Set of p Orbitals

$\psi 2p_{+1} + i\psi 2p_{-1}$	$2p_x$	$\frac{1}{2^5\pi}(z/a)^3\sigma^2 e^{-\sigma}\begin{cases}\sin^2\theta\cos^2\phi\\ \sin^2\theta\sin^2\phi\\ \cos^2\theta\end{cases}$
$\psi 2p_{+1} - i\psi 2p_{-1}$	$2p_y$	
$\psi 2p_0$		

An Alternative Orthogonal Set of d Orbitals

$\psi 3d_0$	$3d_{z^2}$	$1/2.3^8\pi(z/a)^3\sigma^4 e^{-(2\sigma/3)}\begin{cases}{}^1/_3(3\cos^2\theta-1)^2\\ 4\sin^2\theta\cos^2\theta\cos^2\phi\\ 4\sin^2\theta\cos^2\theta\cos^2\phi\\ \sin^4\theta\sin^2 2\phi\\ \sin^4\theta\cos^2 2\phi\end{cases}$
$\psi 3d_{+1} + i\psi 3d_{-1}$	$3d_{xz}$	
$\psi 3d_1 - i\psi 3d_{-1}$	$3d_{yz}$	
$\psi 3d_{+2} + i\psi 3d_{-2}$	$3d_{xy}$	
$\psi 3d_{+2} - i\psi 3d_{-2}$	$3d(x^2-y^2)$	

where $\sigma = \frac{Zr}{a}$ and $a = \frac{h^2}{4\pi^2 mc^2}$

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Charge Enclosed by Contour Surfaces

With a normalized wave function, this becomes a problem in integration of $\psi^*\psi$ over the appropriate limits:

$$f = \text{fraction enclosed} = \iiint_{\text{contour}} \psi^*\psi\, r^2 \sin\theta d\theta d\phi\, dr$$

This equation can be integrated directly when the orbital concerned has spherical symmetry with the limits: $0 < \theta < \pi$, $0 < \phi < 2\pi$ and the values of r defining the contour. In this integration each variable may be treated independently. When the contour surface has a lower symmetry, graphical integration can be used. Even this method becomes quite complex in dealing with an orbital such as the $d_{x^2-y^2}$.

The graphical integration of the carbon $2p_z$ orbital will be described. Since there is cylindrical symmetry around the z axis the integration

$$\int_0^{2\pi} d\phi = 2\pi$$

can be included in the $\psi^*\psi$ function, hence we must evaluate the double integral:

$$f = \iint_{\text{contour}} 2\pi\psi^*\psi r^2 \sin\theta d\theta\, dr$$

In Figure 7 is shown the integral over r (but not θ) as a function of the limiting value of r. This is the area under the curve $2\pi\psi^*\psi r^2$ from 0 to r. At each of the angles 0°, 20°, 40°, 60°, and 70°, the limits of r are

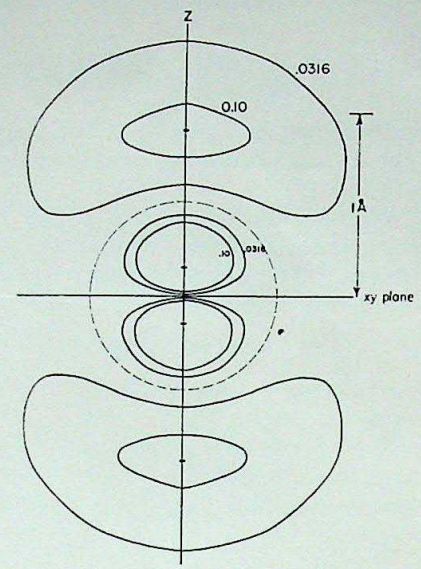


Figure 6. Contours of constant ψ^2 at 0.0316 and 0.10 of maximum for a Cl $3p_z$ orbital. The xy plane and a sphere of radius 0.52 Å are nodal surfaces.

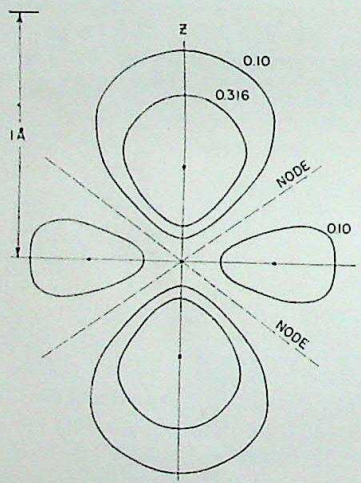


Figure 4. Contours of constant ψ^2 at 0.10 and 0.316 of maximum for a Ti(III) $3d_{z^2}$ orbital in any plane which includes the z axis. The nodes are conic surfaces making an angle $\approx 55°$ with the z axis.

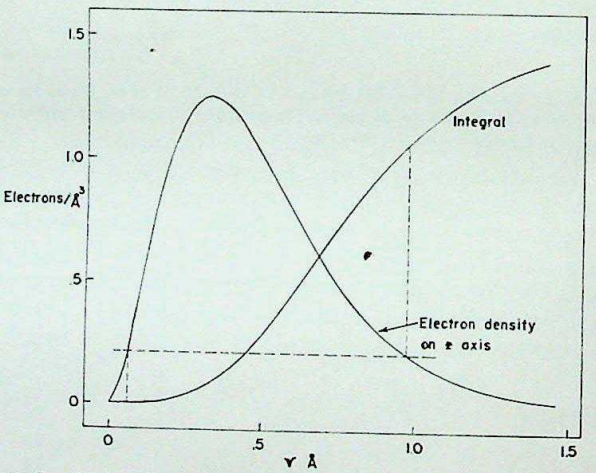


Figure 7. Electron density in a C $3p_z$ orbital along the z axis and the value of the integral $2\pi\int_0^r (\psi(r))^2 r^2 dr$ along the z axis for this orbital.

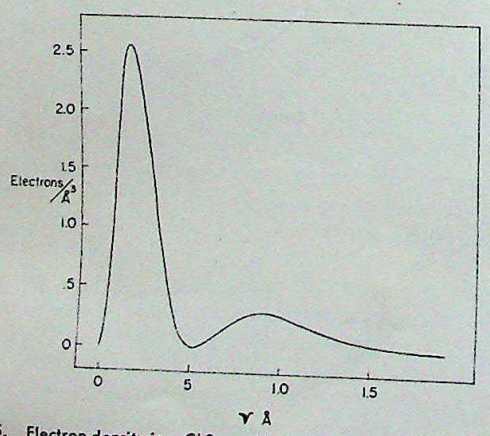


Figure 5. Electron density in a Cl $3p_z$ orbital along the z axis.

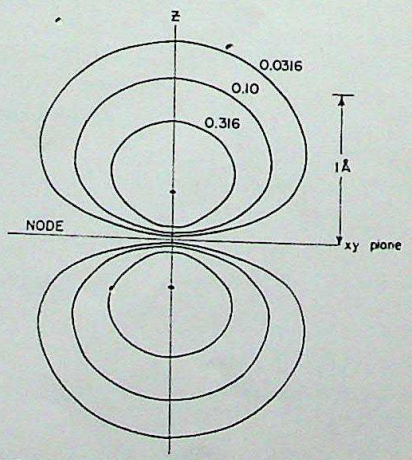


Figure 8. Contours of constant ψ^2 at 0.0316, 0.10 and 0.316 of maximum for a C $2p_z$ orbital. The xy plane is a nodal surface.

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found from the electron density curve of Figure 7, and then the integral over r obtained at that angle. For example, at $\theta = 40°$, with a contour at 0.10 of $\psi^*\psi_{max}$ the limits of r are found by drawing a horizontal line at 0.10 $(\psi^*\psi_{max}/\cos^2 40°) = 0.213$ (dashed line in Fig. 7). The limits of r are thus found to be 0.065 and 0.975 Å. Transferring these limits to the area curve, we find

$$A(\theta = 40°) = 2\pi \int_{r=0.065}^{0.975} \psi^*\psi r^2 dr = 1.07 - 0 = 1.07$$

Now this function is to be integrated over the angle θ:

$$f = \int_0^{\pi} A(\theta)\cos^2\theta \sin\theta d\theta = -\int_0^{\pi} A(\theta)\cos^2\theta d(\cos\theta)$$

This is accomplished by multiplying each value of $A(\theta)$ found from Figure 7 by $\cos^2\theta$ and plotting the result against $\cos\theta$. In Figure 9 the resulting curves for contours at 0.316, 0.10, 0.0316, and 0.00 are shown. The last is included to provide a check on the method since with normalized wave functions, the final integration in this case must yield unity. The integration of these curves gives the fraction of the total electronic charge within a specific contour surface (the areas in Fig. 9 are to be doubled since the graph only extends from 0 to $\pi/2$ rather than to π). The results are 0.34, 0.66, 0.85, and 1.01, respectively, the last value indicating that the method is satisfactory. A smooth curve can be drawn through these points (Fig. 10), from which we find that to include 99% of the charge, a contour surface at $\psi^*\psi = 0.002\psi^*\psi_{max}$ would be required. This contour intersects the z axis at about $r = 2$ Å. This number provides an interesting comparison with the van der Waals radius of carbon of about 1.7 Å.

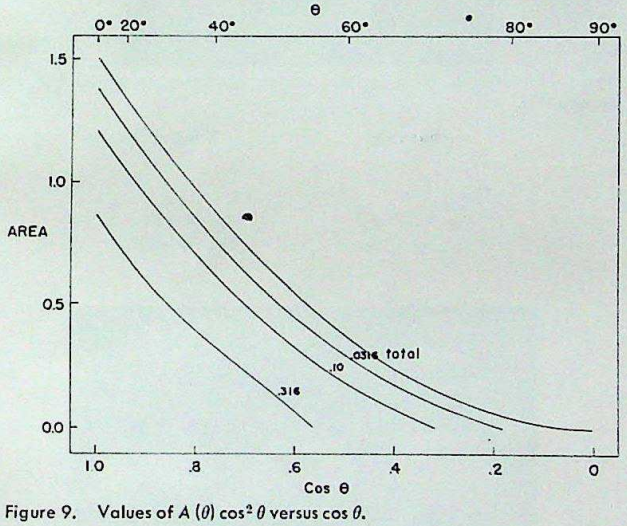


Figure 9. Values of $A(\theta)\cos^2\theta$ versus $\cos\theta$.

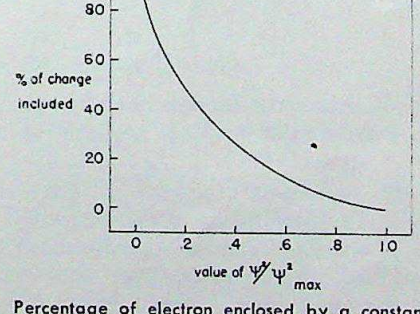


Figure 10. Percentage of electron enclosed by a constant ψ^2 contour versus the values of ψ^2/ψ^2 max.

Atomic Orbital Models

Three dimensional models illustrating the contours described in the previous sections can easily be fashioned from styrofoam. Models of some orbitals of chemical interest are shown in Figure 11. Such models suffer from the disadvantage of not displaying the presence of some nodes (in the 2s and 3s orbitals for example) and also not showing the positions of highest electron density.

Figure 12 shows how it is possible to overcome these deficiencies by cutting wedges out of the models. Areas of low electron density can then be darkened.[1] The contours in Figure 12 represent the complete set of orthogonal orbitals which can be identified with the quantum numbers n, 1 and m_1 for $n = 1$, 2, and 3. They are the orbitals obtained by the method of solution described by Pauling and Wilson in which the

[1] On these models black spray paint was used on the outside and a black marking pencil was used to darken the interior.

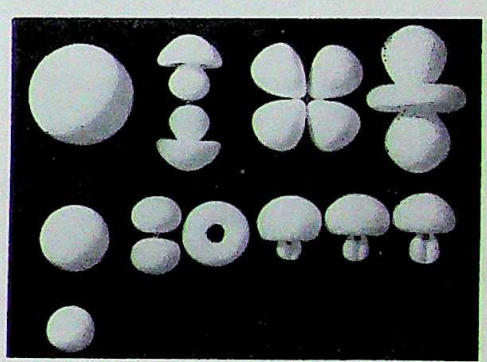


Figure 11. Models of constant ψ^2 contfours of atomic orbitals or the hydrogen atom.

3s	$\begin{pmatrix}3p_x, 3p_y\\ 3p_z \text{ or } 3p_0\end{pmatrix}$	$\begin{pmatrix}3d_{x^2-y^2}, 3d_{xy}\\ 3d_{xz} \text{ or } 3d_{yz}\end{pmatrix}$	$(3d_{r^2}$ or $3d_0)$		
2s	$\begin{pmatrix}2p_x, 2p_y\\ 2p_z \text{ or } 2p_0\end{pmatrix}$	$(2p_{+1}$ or $2p_{-1})$	2sp	2sp^2	2sp^3
1s					



Figure 12. Atomic orbital models which have been cut away to show the presence of hidden nodes and positions of maximum electron density.

3s	3p_0	3$p_{\pm1}$	3d_0	3d_{+1}	3d_{+2}
2s	2p_0	2p_{+1}	2p_{-1}		
1s					

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variable (r, θ, and ϕ) are assumed separable (*5*). Since other orbitals which can be obtained by taking linear combinations of these are useful for the description of polyatomic structures, they are given in Figures 13 and 14 as alternative orthogonal sets of $2p$ and $3d$ orbitals respectively. It is worth noting that values of the quantum number m_l cannot be identified with most of these orbitals. This is still a very common textbook error.

In Figure 15 somewhat schematic models of the $1s$, $2p$, and $3d$ and $4f$ orbitals are arranged to show how they are related to one another by the addition of successive planar nodes.

Molecular Orbital Models

Molecular orbitals formulated by the linear combination of atomic orbitals (LCAO) approximation are shown in Figure 16. These models are principally useful as guides in demonstrating the symmetry of the orbitals and in providing a general idea of the distribution of electron density. The bonding and antibonding orbitals which are found in first and second period homonuclear diatomic molecules are shown. The two types of π orbitals are analogous to the atomic p_0 and $p_{\pm 1}$ orbitals. In a non-linear polyatomic molecule for which the nuclei define a reference plane (e.g., ethylene), the $\pi 2p_x$ orbital is the logical one to use, while in linear molecules, the $\pi 2\, p_{\pm 1}$ orbitals with cylindrical charge symmetry around the molecular axis provide a better description.

Even more schematic are the models of molecules shown in Figure 17. Unfortunately models that attempt to show contour surfaces enclosing large fractions of $\psi^*\psi$ cannot show the individual orbitals. On the other hand, contours enclosing small fractions of $\psi^*\psi$ often do not show the build-up of electron density in the region between the nuclei. No actual calculations have been attempted for these models hence, even in one model, the contour surfaces will represent different fractions of the total charge. With these limitations in mind, the models have been cut away to show the σ molecular orbitals around the molecular axis.

All of the molecules in Figure 13 have cylindrical symmetry. The description of cylindrically symmetric π orbitals is possible in most cases by using either the real p_x and p_y atomic orbitals or the complex $p_{\pm 1}$ orbitals in the LCAO description. In the NO molecule, however, one electron occupies an antibonding orbital.

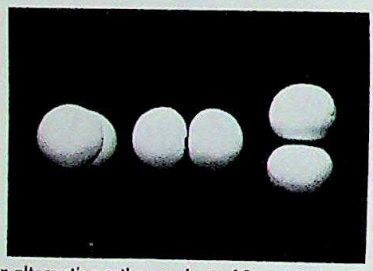


Figure 13. An alternative orthogonal set of $2p$ orbitals.

$2p_z$ $2p_y$ $2p_x$

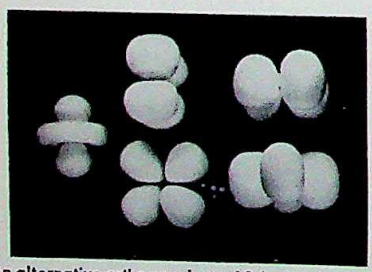


Figure 14. An alternative orthogonal set of $3d$ orbitals.

$3d_{yz}$ $3d_{x^2}$ $3d_{xy}$ $3d_{yz}$ $3d_{x^2-y^2}$

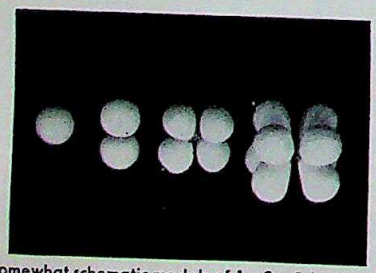


Figure 15. Somewhat schematic models of $1s$, $2p$, $3d$ and $4f$ orbitals.

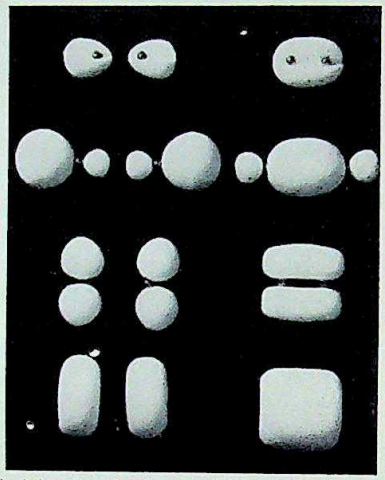


Figure 16. Models of molecular orbitals obtained by the LCAO approximation.

Antibonding	Bonding
σ^*1s	$\sigma 1s$
σ^*2p_z	$\sigma 2p_z$
(π^*2p_x or π^*2p_y)	($\pi 2p_x$ or $\pi 2p_y$)
(π^*2p_{+1} or π^*2p_{-1})	($\pi 2p_{+1}$ or $\pi 2p_{-1}$)

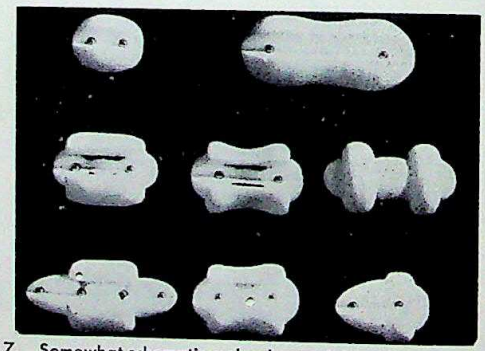


Figure 17. Somewhat schematic molecular models, cut away to show inner orbitals and nuclei.

H_2		Li_2
N_2	O_2	F_2
C_2H_2	NO	HF

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For cylindrical symmetry this must be placed in one of the p_{+1} orbitals. The change in shape of the π contours of the molecules N_2, NO, and O_2 arises from the additional contribution from the π antibonding orbitals, but the bonding and antibonding orbitals cannot, because of overlap, be shown separately (see Fig. 12).

Except for the acetylene molecule, these models have been formulated by the LCAO method without prior hybridization of the atomic orbitals. The point is controversial as indicated in recent calculations showing very little mixing of atomic orbitals even for HF, hence the concept of hybridization is used here only where required for structural reasons.

Acknowledgment

The author would like to express his thanks to Dr. Alan Bree for valuable discussions.

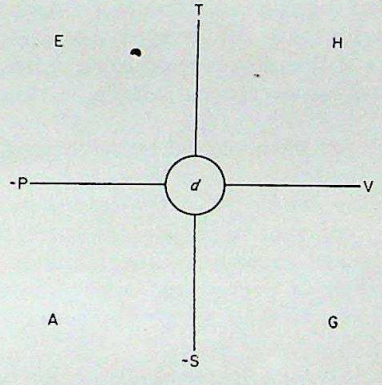
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(1) de Broglie, L., *Ann. de Phys.*, **3**, 22 (1925).
(2) Schrödinger, E., *Ann. d. Phys.*, **79**, 360, 489 (1926); **81**, 109 (1926).
(3) Born, M., *Z. S. Phys.*, **38**, 803 (1926).
(4) Cohen, I., J. Chem. Educ., **38**, 20 (1962).
(5) Pauling, L., and Wilson, E., "Introduction to Quantum Mechanics," McGraw Hill, New York, **1935**.
(6) Slater, J. C., "Quantum Theory of Matter," McGraw-Hill, New York **1953**. Chap. 6.

Mnemonics for Thermodynamic Equations

The appearance of the Symposium on the Teaching of Thermodynamics (THIS JOURNAL, October, 1962) has prompted several readers to submit mnemonic devices found useful in helping the beginner to recall the symbolism which expresses the fundamental equations of thermodynamics. We have extracted the essentials from these communications and assume that the readers know both the meaning of the symbols and the equations.

Edward T. Radley, Northwestern State College, Natchitoches, La., suggests



The differentials of quantities in the quadrants is related to the quantities on the bounding axes, e.g.:

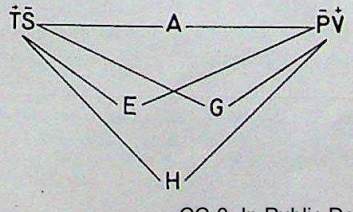
$$dG = -SdT + VdP$$

Also such relationships as:

$$-P = \left(\frac{\partial E}{\partial V}\right)_S = \left(\frac{A}{V}\right)_T$$

follow consistently around the wheel.

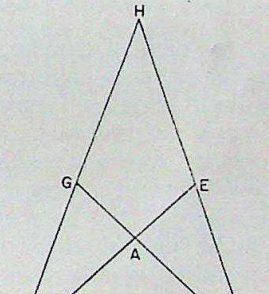
Irwin Cohen, Youngstown University, Youngstown, O., suggests the triangle:



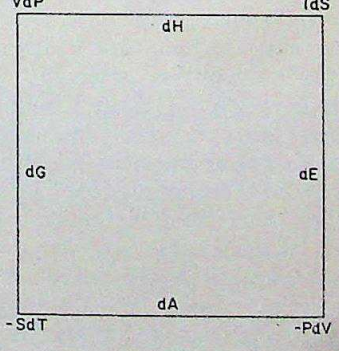
Each term on the second line is the sum of the two above it; H is the sum of all three on the first line. The connecting lines develop the differential equations, using the indicated signs, e.g.,

$$dA = -SdT - PdV \text{ or } dH = TdS + VdP$$

Brother Thomas McCullough, CSC, St. Edward's University, Austin, Tex., suggests the use of a triangular form:



The uppermost quantity is the sum of the lower two on any line. Also the rectangle:



relates the differentials so that the term on the midpoint of the sides is the sum of the two terms on the adjacent corners.

Readers long familiar with THIS JOURNAL will recall other similar devices published about 15–20 years ago. For example, see THIS JOURNAL, **23**, 587 (1946).

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Collected by
Alfred B. Garrett
Ohio State University
Columbus

The Flash of Genius, 16

Quantum Theory: Max Planck

In the first part of the 1800's John Dalton gathered the then known information to show that matter is not continuous stuff but is discontinuous and made of discreet particles which he called *atoms*. His conclusions were drawn from rather simple observations about the solubilities of gases in liquids and from quantitative relations in chemical reactions.

But what could be said about the other great entity of the universe, energy? It is of interest in that about 100 years later a German scientist, Max Planck, gathered the then known information about radiant energy and concluded that it too could be treated as though it were discontinuous stuff and was composed of little bunches of energy which he called *quanta*. His conclusions were drawn because scientists had failed to explain the cause of the wide distribution in wave lengths of radiant energy emitted from a hot body. He reduced their complex equations to a very simple one, $E = h\nu$.

In 1900 three interesting problems were being studied: the structure of atoms that Dalton had postulated; the cause of the lines that Bunsen discovered about 1860 in the spectra of elements; and the nature of radiant energy.

Planck tackled the third problem. Up to that time several mathematical equations had been derived to attempt to describe the distribution of radiant energy from a hot body, but no equation was satisfactory over the entire energy range. In his 1920 Nobel Prize address Planck described his work as follows:[1]

"When I recall the days of twenty years ago, when the conception of the physical quantum of 'action' was first beginning to disentangle itself from the surrounding mass of available experimental facts, and when I look back upon the long and tortuous road which finally led to it, the whole development strikes me as a new illustration of Goethe's saying, that 'man errs, so long as he is striving.' All the mental effort of an assiduous investigator must indeed appear vain and hopeless, if he does not occasionally run across striking facts which form incontrovertible proof of the truth he seeks, and which show him that—after all—he has moved at least one step nearer to his objective. The pursuit of a goal, the brightness of which is undimmed by initial failure, is an indispensable condition, though by no means a guarantee, of final success.

"In my own case the long-time goal was to solve the problem of the distribution of energy in the normal spectrum of radiant heat. Gustav Kirchhoff's discovery (in an enclosure surrounded by emitting or absorbing bodies at the same temperature, the quality of the heat radiation produced is entirely independent of the nature of those bodies) *established the existence of a universal function which depends only upon the temperature and wavelength and is entirely independent of the particular properties of the substance.* The discovery of this remarkable function promised a deeper insight into the relation between energy and temperature. To understand this relationship is the principal problem of thermodynamics and therefore also of the entire field of molecular physics. To find such a function meant to search among all the different bodies occurring in nature, to select one which had known emissive and absorptive powers, and to calculate the energy distribution in the heat radiation that was in equilibrium with the body. This distribution should then, according to Kirchhoff's law, be independent of the nature of the body."

Planck's first attempt was to derive a mathematical equation of two terms for radiant energy, but he was concerned about the lack of physical meaning of the equation.[2]

"Even if this radiation formula should prove to be absolutely accurate it would, after all, be only an interpolation formula found by happy guesswork, and would thus leave one rather unsatisfied. I was therefore occupied from the day of its origination with the task of giving it a real physical meaning. This question led me along Boltzmann's line of thought to consider the relationship between entropy and probability. After some weeks of the most intense work of my life, clarity dawned, and an unexpected view was revealed in the distance."

Planck describes in general terms some of his reasoning in deriving the equation, $E = h\nu$.[3]

"Much less simple than the interpretation of the Boltzmann constant was the interpretation of the second universal constant of the radiation law which, as the product of energy and time (amounting on a first calculation to 6.55×10^{-27} erg-sec), I called the elementary *quantum of action*."

Then he became concerned about tests of his new formula and he said, "While this constant was absolutely indispensable for the attainment of a correct expression for entropy—for only with its aid could the magnitude of the 'elementary region' or 'range' of probability for the statistical treatment be determined—it obstinately withstood all attempts at fitting it, in any suitable form, into the frame of classical theory.[4]

"The first advance in this field was made by Einstein, who on the one hand pointed out that the introduction of the quanta of energy associated with the quantum of action seemed capable of explaining readily a series of remarkable properties of light action discovered experimentally, such as Stoke's rule, the emission of electrons,

[1] Planck, M., "The Origin and Development of the Quantum Theory," Nobel Prize address delivered before the Royal Swedish Academy of Science at Stockholm, June 2, 1920, Oxford, Clarendon Press (1922).

[2] Darrow, K. K., *Sci. Am.*, 186, No. 3 pp. 47–54 (1952).

[3] Planck, M., *Ann. Physik.*, 4, pp. 553–563 (1901).

[4] Planck, M., *Prussische Akademie der Wissenschaftern*, p. 723 (1911, II).

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and the ionization of gases, and later by Planck, by the identification of the expression for the energy of a system of resonators with the energy of a solid body, derived a formula for the specific heat of solid bodies which on the whole represented it correctly as a function of temperature, more especially exhibiting its decrease with falling temperature. A number of [illegible] thus thrown out in different directions, of which the accurate and many-sided investigations yielded, in the course of time, much valuable material. It is not my task to give an even approximately complete report of the successful work achieved in this field, but to give the most important and characteristic phase of the progress of the new doctrine."

Barton Milligan
University of Mississippi
University

A Thermistor Actuated Proportional Temperature Controller

The utility of thermistors, which offer sensitivity, small size, and stability, as temperature sensing and controlling devices[1] has been widely recognized in recent years. Although the advantages of continuous (or proportional) temperature control, in which heater power is continuously adjusted according to need rather than switched completely on or off, have been recognized[2] for some time, the cost of continuous controllers has been high.

The high sensitivity of thermistors compared to metallic resistance thermometers and thermocouples permits thermistor based devices to be relatively simple. We have assembled, from parts costing about $50, a thermistor actuated continuous control employing only solid state devices. The circuit, shown in the figure, can be easily installed in a 5-× 7-× 2-in. or even smaller chassis. The circuit as given, which is derived from suggestions made by a manufacturer of silicon controlled rectifiers,[3] will control up to 400 watts, but by means of modifications adding approximately $30 to the cost of parts its capacity can be increased to over a kilowatt without sacrificing sensitivity. However, a source of detailed information should be consulted before any changes are attempted.

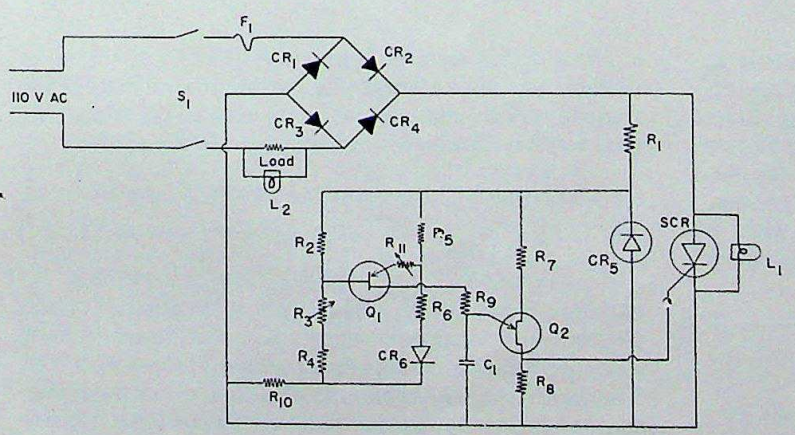
Our controller is less sensitive than some proportional devices[2]; a change of 0.3°C of the thermistor is required to change the control from "on" to "off." However, it maintains a well stirred 5-gal. water bath at ±0.05°C or better for extended periods. Therefore, its compactness, stability and ruggedness are its principal advantages over conventional controls of comparable cost.

The heart of the circuit is the silicon controlled rectifier (SCR), which is roughly a solid state analogue of a thyratron tube but has many times the power

[1] Ratcliffe, J. S., J. Chem. Educ., 39, 637 (1962); Lewin, S. Z., J. Chem. Educ., 36, A199 (1959).

[2] Sturdevant, J. M., "Technique of Organic Chemistry," Weissberger, A., edit., 3rd ed Interscience Publishers, New York, 1960, Vol. 1, p. 1 ff.

[3] Gutzwiller, F. W., Jones, D. V., Lowry, H. R., Sylvan, T. P., and Van Zastrow, E. E., "Controlled Rectifier Manual," 1st ed., Semi-conductor Products Dept., General Electric Co., Liverpool, New York, 1960, p. 90 ff.; Malmstadt, H. V., Enke, C. G., and Toren, E. C., Jr., "Electronics for Scientists," W. A. Benjamin, Inc., New York, 1962, pp. 384–488.



Parts List

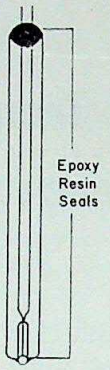
S_1 Switch
F_1 Fuse 4 amp (because of the sensitivity of SCR's to transients, the fuse should be of the current limiting type, for example, Buss "Limitron" or Chase-Shawmut "Amp-Trap")
SCR 2N1774A, CR_1-CR_4 6F20 Mounted on cooling fin
CR_5-1N1527, CR_6-1N91
Q_1 2N525, Q_2 2N491
C_1 0.01 mfd
R_1 1500 10 watt
R_2 Thermistor, 10–20°K in range of use (Veco 41 A 11 near 25°C), see text
R_3 Multiturn potentiometer to match R_2, low temperature coefficient
R_4 100 #1/2 watt, low temperature coefficient
R_5, R_6 300 #1/2 watt, low temperature coefficient[a]
R_7 470 #1 watt, R_8 47 #1/2 watt, R_9 2.2K #1/2 watt, R_{10} 10002 watt
R_{11} 250 wirewound (sensitivity control)
L_1, L_2 3 watt, 120 V panel lamp, (1 red, 1 green)

[a] The sensitivity of the controller can be approximately doubled by replacing R_6 with a thermistor similar to R_2 and replacing R_5 with a fixed resistor matching R_6.

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capacity at comparable cost. Within its design limits the SCR is normally non-conducting in either direction. If current of sufficient magnitude passes between the gate (control electrode) and the cathode while the cathode is negative, the SCR becomes conducting and remains so (even though the gate signal is removed) as long as the current remains above a certain value, called the holding current. Once forward current has fallen below the holding current, as will occur at the end of an ac cycle, the SCR becomes blocking again and will not conduct until a signal is again applied to the gate while the cathode is negative. In our controller full wave rectified ac, from CR_1-CR_4, is applied across the SCR and the load in series. This arrangement offers a number of advantages.[3] The control circuit operates as follows: The zener diode, CR_5, breaks down at 22v, providing essentially a rectified square wave potential across the remainder of the circuit. The power resistor R_1 serves to limit the current through CR_5. Resistances R_2-R_6 comprise a Wheatstone bridge. When the temperature of the thermistor (R_2) is too low, the unbalance signal of the bridge is amplified and converted to a pulse by the system Q_1, Q_2, C_1, R_8, and R_9 during each cycle. The timing of the pulse during the cycle is determined by the magnitude of unbalance signal. The greater the unbalance the sooner in the cycle the pulse, which fires the SCR, is generated. If the temperature of the thermistor is too high, the unbalance signal is of the wrong polarity to be amplified, and no firing pulses are generated. The resistance R_3 is adjusted to set the operating temperature. Any multiturn potentiometer having a reasonably low temperature coefficient of resistance will suffice. Because the temperature setting is seldom altered in our use, we have employed a 25 turn miniature trimming potentiometer having a screwdriver adjustment. The resistance R_4 is used to match R_3 to the thermistor, R_2. It also prevents a runaway condition in case R_3 is accidentally set to zero resistance. The fixed resistances R_5 and R_6 should also have low temperature coefficients and reasonable values (we have used 300 ohms). One of the great advantages of the high sensitivity of thermistors is apparent here. For this application standard high quality resistances can be employed, whereas in similar circuits employing metallic resistance thermometers special resistances having extremely low temperature coefficients must be employed. The diode CR_6 serves to compensate for changes in the characteristics of Q_1, with temperature.



The thermistor can be of any type, but for liquid bath control the bead-sealed-in-glass probe type seems to be best. The sensitivity of the instrument is unaffected by the total resistance of the thermistor for a given thermistor characteristic. However, because of the tendency of the thermistor to be self-heated by the current passing through it, the higher its resistance the better. We have chosen, as a compromise, to use thermistors having resistances of 10–20 kohms at the temperature of the bath.

Thermistors as supplied are small and fragile and must be mounted. We have found that a bead in glass type thermistor sealed into a 6 or 8 mm glass tube with epoxy cement, as shown in the figure is as rugged and convenient to use as a laboratory thermometer. The relative intensities at which lamps L_1 and L_2 glow are an indication of the "on-off" proportions. Alternatively, the "on-off" proportions can be indicated by omitting L_1 and replacing L_2 with a small, inexpensive ac voltmeter. Details of construction will be supplied to interested persons.

This controller was developed in the course of work supported by the Petroleum Research Fund administered by the American Chemical Society. Grateful acknowledgment to the donors is hereby given.

Robert D. Whitaker[1]
Washington and Lee University
Lexington, Virginia

A Kinetics Experiment for the Physical Chemistry Laboratory

This paper describes an experiment in chemical kinetics in which the absorbance of a reacting species is determined as a function of time. The experiment may easily be completed in one or two three-hour laboratory periods with sufficient information to enable the calculation of the activation energy. The results reported herein were obtained with a Beckman Model DB Spectrophotometer, using silica cells with a thickness of 1 cm.

Basolo, Hayes, and Neumann[2] studied the rate of dissociation of the tris-*o*-phenanthroline nickel(II) ion in acidic solution. These workers found that the complex ion dissociates in a stepwise fashion:

$$\text{Ni}(o\text{-phen})_3^{++} \xrightarrow{k_1} \text{Ni}(o\text{-phen})_2^{++} + o\text{-phen}$$

$$\text{Ni}(o\text{-phen})_2^{++} \xrightarrow{k_2} \text{Ni}(o\text{-phen})^{++} + o\text{-phen}$$

$$\text{Ni}(o\text{-phen})^{++} \xrightarrow{k_3} \text{Ni}^{++} + o\text{-phen}$$

with $k_1 < k_2 << k_3$. $\text{Ni}(o\text{-phen})_3^{++}$, $\text{Ni}(o\text{-phen})_2^{++}$, and $\text{Ni}(o\text{-phen})^{++}$ represent the "tris," "bis," and "mono" *o*-phenanthroline complexes of nickel(II), respectively. The k_1, k_2, and k_3 represent the first order rate constants for the consecutive first order reactions. It was

[1] Present address: Department of Chemistry, The University of South Florida, Tampa, Florida.

[2] Basolo, F., Hayes, J. C. and Neumann, H. M., *J. Am. Chem. Soc.*, 75, 5102–6 (1953).

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found that k_2 exceeds k_1 by about a factor of ten, so that the first step is rate determining. In order to prevent the opposing reactions involving the recombination of the *o*-phenanthroline with the ions, the reaction is run in moderately concentrated HCl solution. The free *o*-phenanthroline immediately combines with a proton to give a species which will be represented, *o*-phenH$^+$.

In general, the absorbance at any time is given by:

$$A = a_{tris}[Ni(o\text{-phen})_3^{++}] + a_{bis}[Ni(o\text{-phen})_2^{++}] + a_{mono}[Ni(o\text{-phen})^{++}] + a_{Ni^{++}}[Ni^{++}] + a_{o\text{-phenH}^+}[o\text{-phenH}^+] \quad (1)$$

where A is the absorbance, the a's are the appropriate absorptivities, and the brackets indicate molar concentrations of the various species in solution. Equation (1) is greatly simplified by a proper choice of wavelength at which the absorbance is measured. At 420 mμ, a simple expression results because a_{tris} is much larger than the other absorptivities at this wavelength. The term $a_{o\text{-phenH}^+}$ is essentially zero at 420 mμ. Also, since the initial step is rate determining, the concentration of the "bis" and "mono" complexes will be much smaller than the concentration of the "tris" complex during the initial stages of the reaction when the "tris" concentration is relatively large. At 420 mμ, the absorbance is thus given to a good approximation

$$A = a_{tris}[Ni(o\text{-phen})_3^{++}] \quad (2)$$

Ni $(o\text{-phen})_3^{++}$ dissociates by a first order reaction so

$$[Ni(o\text{-phen})_3^{++}] = [Ni(o\text{-phen})_3^{++}]_0 e^{-k_1 t} \quad (3)$$

where $[Ni(o\text{-phen})_3^{++}]_0$ is the initial concentration of the "tris" complex and t is the reaction time expressed most conveniently in minutes. Combining equations (2) and (3),

$$A = a_{tris}[Ni(o\text{-phen})_3^{++}]_0 e^{-k_1 t} \quad (4)$$

Taking natural logarithms of both sides of equation (4),

$$\ln A = \ln(a_{tris}[Ni(o\text{-phen})_3^{++}]_0) - k_1 t \quad (5)$$

Converting natural logarithms to common logarithms,

$$\log A = \log(a_{tris}[Ni(o\text{-phen})_3^{++}]_0) - 0.434 k_1 t \quad (6)$$

According to equation (6), a plot of log A versus t should give a straight line with a slope of $-0.434k_1$.

Equation (6) holds fairly well for about 1–2 hours after the reaction begins, depending upon the temperature at which the reaction is carried out. Since the value of k_1 is determined solely by the slope of the line, the initial concentration of the "tris" complex is unimportant.

The Experiment. About 0.25 g of $Ni(o\text{-phen})_3Cl_2 \cdot 7H_2O$ is dissolved in 25 ml of 5 M HCl which has been thermostatted for about 20 minutes at 25.0° ± 0.1° (or any other convenient temperature). The solution is returned to the thermostat with occasional shaking for five minutes. A small sample is withdrawn and its absorbance at 420 mμ measured, using 5 M HCl as the reference. Thereafter at 20–30 minute intervals, samples are withdrawn and their absorbance at 420 mμ measured. Readings are continued for about $1^1/_2$ hours. Another sample is run at a temperature about 8° higher (or lower) than the first run. If the higher temperature is used, the readings should be taken every 20 minutes for about an hour. If the lower temperature is used, the readings should be taken every 30 minutes for about two hours. The logarithm of absorbance is plotted as a function of the time in minutes for each temperature. It is convenient to take the first reading as zero time. The best straight lines are drawn through the points for each temperature and the rate constants determined from the slopes of the lines by:

$$k_1 = -\frac{\text{slope}}{0.434} \quad (7)$$

Duplicate runs should be made at each temperature if time permits and the most consistent sets of data used. The activation energy is then determined from the values for k_1 at the two temperatures by:

$$E_a = \frac{2.3 \times 1.99 \times T_1 T_2}{T_2 - T_1} \log \frac{k_1(2)}{k_1(1)} \quad (8)$$

The $Ni(o\text{-phen})_3Cl_2 \cdot 7H_2O$ may be supplied the students, or each student or student pair can easily prepare their own samples by following the directions of Pfeiffer and Tappermann.[3]

0.20 g $NiCl_2 \cdot 6H_2O$ and 0.60 g *o*-phenanthroline are dissolved in 10 ml warm distilled water. The resulting raspberry-red solution is evaporated over a steam bath until crystals begin to form on the surface of the solution. Crystallization then proceeds for about an hour at room temperature after which the crystals are collected on a Büchner funnel. The yield is 0.6–0.7 g of damp crystals which are ready for immediate use since the initial concentrations need not be known.

Results. Student data for two temperatures are plotted in the figure. Equation (7) is employed to calculate k_1 at the two temperatures:

25.6° $k_1 = 7.8 \times 10^{-4}$ min^{-1}
32.9° $k_1 = 1.8 \times 10^{-3}$ min^{-1}

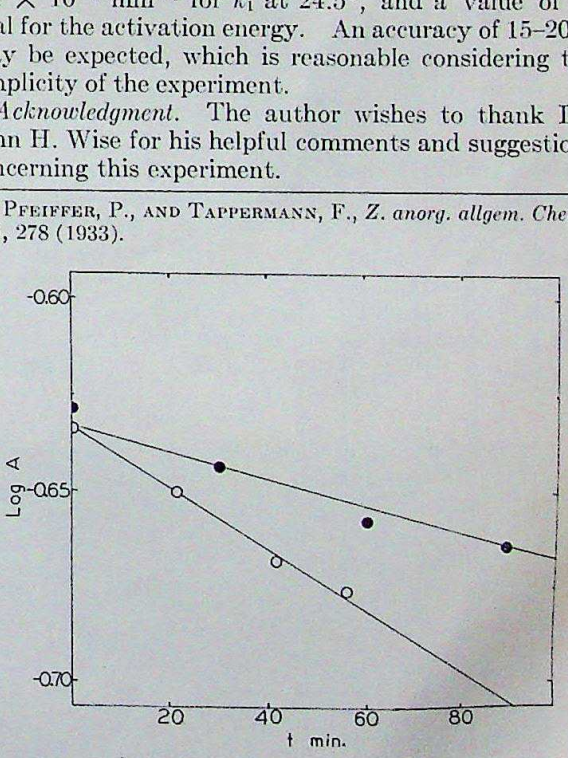
Then by equation (8), the activation energy is found:

$$E_a = 21 \times 10^3 \text{ cal}$$

Basolo, Hayes, and Neumann[2] reported a value of 5.4×10^{-4} min^{-1} for k_1 at 24.5°, and a value of 25 kcal for the activation energy. An accuracy of 15–20% may be expected, which is reasonable considering the simplicity of the experiment.

Acknowledgment. The author wishes to thank Dr. John H. Wise for his helpful comments and suggestions concerning this experiment.

[3] Pfeiffer, P., and Tappermann, F., *Z. anorg. allgem. Chem.*, 215, 278 (1933).



Logarithm of absorbance versus time for two temperatures: —●— 25.6° —○— and 32.9°.

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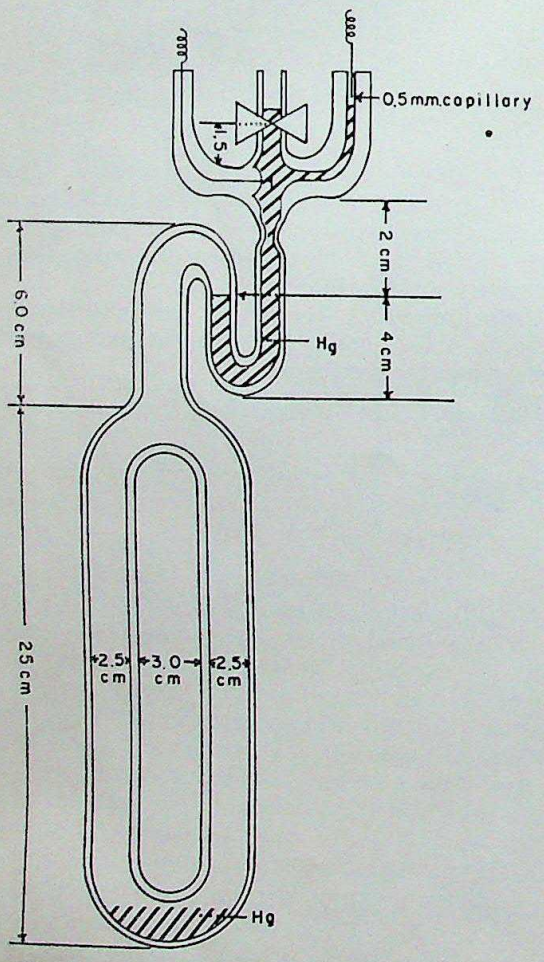
Sam Katz[1]
Naval Medical Research Institute
Bethesda, Maryland

A Simple Thermoregulator

A heptane-mercury thermoregulator capable of maintaining temperature constant within 0.002°C between the range of −20° to 50°C is described. It differs from other regulators of similar sensitivity by its simplicity of fabrication, sturdy construction, and ease of filling. It can be made by any individual possessing a minimal proficiency in glass-blowing.

The details of construction are presented in the accompanying figure. The dimensions are not critical, being determined by the geometry of the thermostat.

[1] The opinions or assertations contained herein are the private ones of the writer and are not to be construed as official or reflecting the views of the Navy Department or the naval service at large.



A diagrammatic representation of the heptane-mercury thermoregulator.

A platinum electrode is sealed in one limb so that it is immersed in mercury, while the adjustable stainless steel lead,[2] the fine control, is seated in the capillary. The inner diameter of the thick-walled glass capillary is 0.5 mm.

The unit is charged by initially evacuating the system by applying a vacuum via the capillary with the Teflon stopcock closed. Then the tube leading to the vacuum source is sealed, and heptane is added through the stopcock until it is about 75% filled. From 10 to 30 ml of mercury is put in a layer on the bottom, followed by additional heptane until the solvent reaches the position indicated in the diagram. The final temperature setting is made by adding mercury and adjusting the fine variable lead in the conventional manner.

The sensitivity of a thermoregulator is a function of the volume change produced by a change of temperature and by the rate of heat transfer from the thermostat to the sensing unit and vice versa. This unit capitalizes on the first factor, i.e., employing a large volume, 300 ml, of heptane—a material characterized by a large coefficient of cubical expansion, 1.22×10^{-3}/degree.[3] Consequently a temperature change of 0.001°C will produce a volume change of 0.36 microliters or a change of 1.85 mm in the capillary. Obviously, the thermostatic element would be activated by a smaller temperature change.

However, the primary factor determining the sensitivity of a thermoregulator is the rate of heat transfer. The rate expression for heat transfer due to conduction is as follows:

$$\phi = -KA \frac{dT}{dX}$$

where ϕ is the rate of heat flow across a surface element of area, A, under a temperature gradient, dT/dX where K is the thermal conductivity. Inspection of this equation will reveal that an ideal thermoregulator should expose the maximum possible surface relative to volume and should incorporate materials with high coefficients of expansion, thermal conductivity and thermal diffusivity. It is the last two factors which are the basis for the widespread use of mercury—since it has excellent thermal and electrical conductivity properties. Yet the relatively low coefficient of expansion, 0.18×10^{-3}/ degree, and the high density of mercury impose serious restrictions upon instrument design.

[2] It is essential that the mercury surface be clean, but it is more important still that the mercury should not be wet and adhere to the contact element. The use of "tinned" copper wire is to be avoided for this reason.

[3] "Landolt-Börnstein Physikalisch-Chemische Tabellen," edited by Roth, W. A., and Scheel, K., 5th Auflage, 2 Band, J. Springer, Berlin, 1923, p. 1224.

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To circumvent the use of mercury, one category of thermoregulators employs materials with high coefficients of expansion, such as toluene or heptane. But since these substances are characterized by low thermal conductivity, the apparatus must be designed to maximize the surface area relative to the volume in order to compensate for their poor conductivity. The resultant unit is generally fragile and susceptible to breakage.

In the unit described here, both mercury and heptane are used. Since the density of heptane is low, 0.682 g/ml, the use of thin glass in the circular section of this regulator is permitted, eliminating the thermal lag attributable to glass, a poor thermal conductor. Heat transfer is further facilitated by the mercury on the bottom of the reservoir, due to its excellent thermal conductivity. In addition to the heat transfer affected by conductivity there is some transfer due to convection. The geometry of the circular reservoir promotes the convectional movement of heptane arising from any pensity differences resulting from temperature gradients. The temperature monitored by this regulator is an integrated quantity since it encompasses the entire depth of the thermostat. Thus it cannot be unduly influenced by any localized temperature gradient which might exist in the bath.

The effectiveness of any thermoregulator is the function of a thermostat in which it is employed. Adequate stirring is the single most important factor in determining the efficiency of a thermostat. For optimum performance a minimum of 80% of the heat should be furnished by a constant heat source, with the remainder from a low-lag heater controlled by the thermoregulator. For the latter purpose, a 60 watt bulb, painted black, connected in series with a Variac can be used. By positioning the intermittent heat source about 5 to 7.5 cm away from a thermoregulator, the tendency for a temperature overshoot to occur is virtually eliminated.

The helpful comments of Dr. R. F. Steiner, regarding this apparatus, is acknowledged.

Paul Schatzberg
U. S. Naval Engineering
Experiment Station
Annapolis, Maryland

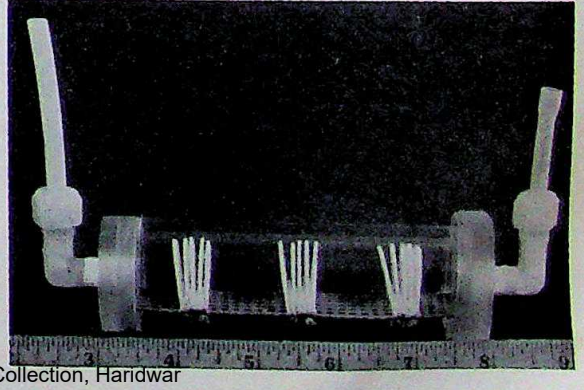
A Gas Saturation Apparatus

The need to saturate air with water or, in general, gases with liquids frequently arises in the laboratory. A simple apparatus for doing this is illustrated in the photograph which shows dimensions and construction features. The apparatus shown was made from clear plastic tubing and nylon fittings. A somewhat simpler construction than that shown uses two number 7 rubber stoppers to close the ends of the large tube. Each stopper was fitted with a right angle bend of glass tubing.

The evaporator section consisted of a stiff metal strip of coarse screen material ($1 \times 4^1/_2$ in.) provided with three or more slots, each of which can accept four or five absorbent (nutrient) pads. These pads are cut so that the portion above the metal screen just clears the inside of the tube. The pads are held apart by strips cut from other pads. The lower portion of each pad fits into slots in the metal screen, projecting below it about $^1/_8$ in. When cut in the described manner, each absorbent pad should look like a two-dimensional projection of a mushroom. The removable press fit cap on one end of the tube holds the screen firmly in place.

Water or another volatile liquid is introduced into the tube until its level reaches the bottom of the screen. This wets the lower portion of the absorbent pads and, by capillary action, the rest of the pads. Air or another gas can be passed through the apparatus from either end.

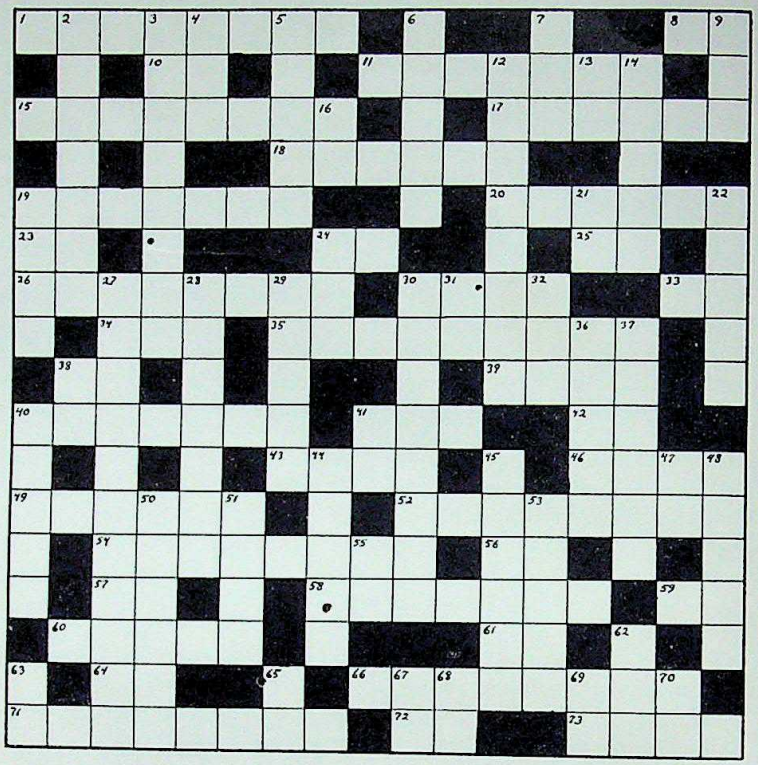
The entire apparatus is easily placed in a constant temperature bath. The saturated gas emerging from the apparatus can be quickly passed through other equipment situated in the same bath. The apparatus can be used singly or in series of two. By varying the bath temperature and gas flow rate, various levels of saturation can be obtained. Since the gas being saturated does not bubble through the liquid, a technique which is frequently used, an undesirable aerosol mist is not formed.



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Chemical Crossword Puzzle



Across

1. Metal with highest melting point
8. Almost always mixed with zirconium
10. Radioactive Group II metal
11. Heavy, heavy hydrogen
15. Substance which changes the rate of a reaction
17. _____ sugar, an equimolar mixture of glucose and fructose
18. Any hydrocarbon with a double bond
19. Lightest of all metals
20. Metal with red and blue chlorides
23. Atomic number 63
24. Only yellow metal
25. Most abundant of the metals in the earth's crust
26. Quartz tinted with manganese impurities
30. Combining form indicating fluorine
33. Very versatile, expensive metal highly resistant to corrosion
34. Prefix meaning new
35. Silver-white, semimetallic member of sulfur family
38. Metal with brilliant yellow sulfide
39. Saint's name in name given to a natural flame-like brush discharge
40. $(CH_3)_2CHCH_2CH_2$—group
41. Prefix meaning not
42. Deep red, volatile liquid
43. Oven in which glassware is annealed
46. To extract or distill
49. Second member of paraffin series
52. Product of destructive distillation of natural rubber
54. Elementary particle of negative electricity
56. Isolated by Mme. Curie in 1911
57. Element with eight electrons in *P* shell but none in *Q* shell
58. Mixture of aluminum and some metallic oxide
59. Product of reduction of CO_2 with hot coke
60. —NH_2 group
61. Fourth member of aluminum family
64. Suffix indicating higher valence state
66. Levulose; fruit sugar
71. Organic substances containing OH group
72. Semimetallic element commonly used in poisons
73. Valence of carbon

Down

2. Currently most important source of atomic energy
3. Soft, slippery, crystalline form of carbon
4. Old chemical word meaning salt
5. Town from which $MgSO_4 \cdot 7H_2O$ takes its common name
6. Process for making wood pulp using NaOH and Na_2S
7. Element with ten stable isotopes
9. Glyceryl ester of long chain acids
12. Medicinal alcoholic solution
13. Ultraviolet
14. Any element which is lustrous and malleable and is a good conductor
16. Softest member of aluminum family
19. Soft, heavy, amphoteric metal
21. Used to color green flares
22. Prefix meaning four
24. Suffix for negative radical containing more oxygen
27. Reaction which absorbs heat
28. Any biochemical which controls vital processes
29. Vessel used in distilling liquids
30. Reacts directly with all elements except N, O, Cl, and inert gases
31. Last rare earth
32. Any unctuous, combustible liquid soluble in ether but not in water
36. Brown pigment of ferric and manganese oxides
37. Determined composition of water with great precision
38. Lowest ionization potential of any element
40. Entering into no chemical reaction
41. Imino group
44. Any of several difficultly reducible metallic oxides
45. Simplest organic acid
47. Indium
48. Densest stable inert gas
50. Common, very strongly magnetic alloy
51. A reflection of sound waves
53. Suspension of a pigment in a drying oil
55. The hydroxyl group
62. Prefix for straight chain ending in $(CH_3)_2CH$—
63. Most abundant alkaline earth metal
65. Greenish-yellow gaseous element
67. Makes luminous paint luminous
68. Country which pioneered development of atomic energy
69. Oxidizing flame
70. The only stable nuclei of mass number 151 or 153.

(*See next issue for solution*)

Ronald A. Schneider
Redlands, California

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Chem Ed

LETTERS

To the Editor:

The article "Ratio Errors in Pseudo First Order Reactions,"[1] points out that when $a > b$, calculation of the pseudo first order constant,

$$k' = k(a - b) = 1/t \ln [b/(b - x)]$$

produces errors in k at the start of the reaction of 20, 10, 4, 2, and 1% for initial a/b ratios of 5, 10, 25, 50, and 100.[1] Although the percent error *falls* as the fraction of reaction of x/b increases, their analysis correctly emphasizes the hazards of obtaining the second order rate constant k from the ratio $k'/(a - b)$.

One can also obtain k from the ratio k'/a. Here the percent error *increases* as x/b increases. Or one can compromise with $k = k'/(a - b/n)$. The accompanying figure gives the pattern of fractional error in k for two a/b ratios and several n as the extent of reaction changes. The fractional error in k is given by

$$F = 1 - c\left(1 + \frac{\ln [(a - x)/a]}{\ln [b/(b - x)]}\right)\frac{(a - b/n)}{(a - b)}$$

This expression presumably can be evaluated by computer for desired values of a/b, n, and x/b. Once a/b and x/b become fixed by the experiment, one n value will minimize the sum of the positive and negative errors.

However, such elaborate calculations are normally superfluous in kinetic studies. Most workers[2, 3] using the pseudo first order technique try to keep $a/b > 10$ and use the expression $k = k'/a$: at $a/b = 10$ and $x/b = 0.8$, the average error in k is then about -2 to -3%. (Occasionally the average value, $a - b/2$, has been used.[4]) For the same a/b and x/b, the calculation of $k = k'/(a - b)$ leads to an average error of 7–8%. Therefore, we suggest that most pseudo first order kinetic studies will not contain errors as large as those predicted.[1]

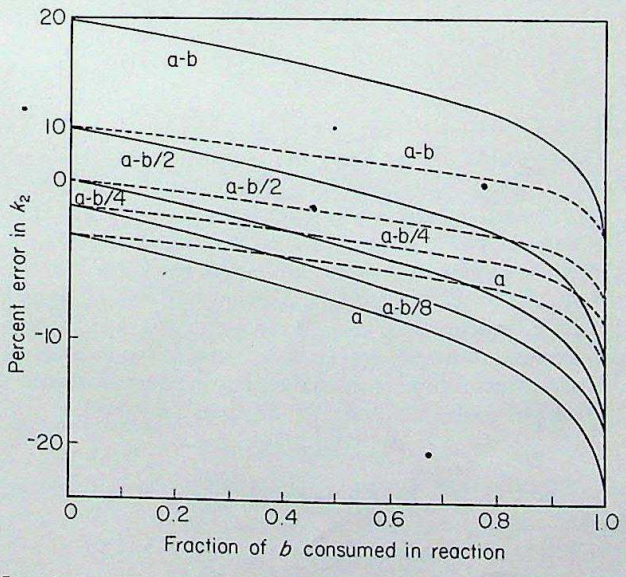
R. A. More O'Ferrall and Sidney I. Miller
Illinois Institute of Technology
Chicago, Illinois

[1] Sicilio, F., and Peterson, M. D., J. Chem. Educ., **38**, 576 (1961).

[2] Ciapetta, F. G., and Kilpatrick, M., *J. Am. Chem. Soc.*, **70**, 639 (1948).

[3] Roberts, J. D., and Regan, C. M., *Anal. Chem.*, **24**, 360 (1952).

[4] Alberry, S. J., and Bell, R. P., *Trans. Faraday Soc.*, **57**, 1942 (1961).



Error in the calculated value of a second-order rate constant obtained by dividing the pseudo unimolecular rate constant by various functions of the initial concentration as indicated on the curves. Full lines have $a/b = 5$; broken lines have $a/b = 10$.

To the Editor:

One of the conclusions of Haas and Gayer in their recent article (this Journal, **39**, 537 (1962)) was, "If it turns out that there are only $(n - 2)$ mathematical equations available for n coefficients of a chemical equation, it is impossible to balance a reaction without applying some knowledge of chemistry."

Application of Diophantine linear analysis to these indeterminate equations can separate simultaneous reactions and also define side reactions, as follows:

$$a\text{Cu} + b\text{HNO}_3 \rightarrow a\text{Cu(NO}_3)_2 + c\text{NO} + d\text{H}_2\text{O} + e\text{NH}_2\text{OH}$$

The material balance is

$$\text{H}: b = 2d + 3e \quad (1)$$

$$\text{N}: b = 2a + c + e \quad (2)$$

$$\text{O}: 3b = 6a + c + d + e \quad (3)$$

Eliminating b between equations (2) and (3) gives

$$2c + 2e = d \quad (4)$$

Substituting this value of d into equation (3) gives

$$b = 2a + c + e \quad (5)$$

Equating equation (1) to equation (5), and by substitution from equation (4)

$$3c + 6e = 2a \quad (6)$$

This substituted into equation (2) gives:

$$b = 4c + 7e \quad (7)$$

Substituting for the reaction these coefficients:

$$(3c + 6e)\text{Cu} + (8c + 14e)\,\text{HNO}_3 \rightarrow (3c + 6e)\text{Cu(NO}_3)_2 + 2c\text{NO} + (4c + 4e)\text{H}_2\text{O} + 2e\text{NH}_2\text{OH}$$

Since c and e are the only independent variables, let $c = 1$, $e = 0$; and $c = 0$, $e = 1$. We have either

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$$3Cu + 8HNO_3 \rightarrow 3Cu(NO_3)_2 + 2NO + 4H_2O$$

or

$$6Cu + 14HNO_3 \rightarrow 4H_2O + 6Cu(NO_3)_2 + 2NH_2OH$$

Eliminating Cu algebraically

$$HNO_3 + NH_2OH \rightarrow 2NO + 2H_2O$$

In $(n - x)$ simultaneous linear equations involving n variables, there will be only x independent variables, $(n - x)$ linearly dependent variables, x main reactions, and $(2^x - x - 1)$ side reactions. This technique might be used in complex industrial organic processes of low yield, if all products can be identified.

DONALD R. SWAYZE

47 SAYRE STREET
ELIZABETH, NEW JERSEY

To the Editor:

Because of the rapid advances in chemistry in recent years the vocabulary used to describe new terms has been often vague and inadequate. In order to correct and revise one frame of reference, may I offer—at the instigation of Dr. Naeser of George Washington University—the use of the word "ionocule" for the opposite of molecule. Certainly the present use of "formula" or "nonmolecular" is anything but satisfactory for substances which are empirical. The former term suggests that molecules have no formulas; and the latter intimates what the substance is not, but certainly *not* what it is. As a teacher I find it increasingly difficult to cope with the poor choice of words in the field of chemistry. I hope a keen awareness of this situation will bring forth more descriptive and better suited vocabulary to our branch of science.

CHARLOTTE LINDE

WAKEFIELD HIGH SCHOOL
ARLINGTON, VIRGINIA

To the Editor:

W. E. Dasent in his article on "Non-existent Compounds" (THIS JOURNAL, **40**, 130 (1963)) commented, "In view of the exceptional electronegativity of fluorine and the high polarity of the C-F bond, it is surprising that substances containing hydrogen bonds such as R_3C-F...H-OR do not seem to have been prepared." Actually, several reports of hydrogen bonding involving alkyl monofluorides are available in the literature (SCHLEYER, P. VON R., AND WEST, R., *J. Am. Chem. Soc.*, **81**, 3164 (1959); WEST, R., POWELL, D. L., WHATLEY, L. S., LEE, M. K. T., AND SCHLEYER, P. VON R., *J. Am. Chem. Soc.*, **84**, 3221 (1962) and the references cited therein) but such associations are relatively weak. Hydrogen bonds between phenol and cyclohexyl fluoride ($-\Delta H^\circ = 3.1$ kcal/mole) are only slightly stronger than phenol...cyclohexyl iodide ($-\Delta H^\circ = 1.7$ kcal/mole) and for example, even inferior in strength to phenol . . . di-*n*-butyl selenide ($-\Delta H^\circ = 3.7$ kcal/mole). Neither the "exceptiona[electronegativity of fluorine" nor "the high "polarity of the C-F bond" apparently is of paramount importance in determining hydrogen bond enthalpies.

PAUL VON R. SCHLEYER

PRINCETON UNIVERSITY
PRINCETON, NEW JERSEY

To the Editor:

We have numerous institutes devoted to upgrading science teaching. My experience suggests that some attention needs to be given to upgrading communication skills. I was disillusioned when ninety-eight spelling errors appeared on a short-answer midterm in an NSF course for science teachers.

Using the spelling which appeared on this exam, the science teachers might produce the following exposition on water and hydrogen.

Water is *amhyroteric*, is highly *poler*, and has a high *service tention*. It is less *volitila* than its *emphirical* formula indicates. Water vapor condenses on a cold surface to form *due*. The loss of water by a hydrate is called *eflouresense* and the opposite process is called *deliquensence*. Water contains hydrogen which is a *gass*. Light hydrogen contains no *nutrons* but its heavier *isotropes* do. Hydrogen forms *hydrieds*. Hydrogen atoms undergo *neclear fussion* to form helium. Hydrogen atoms may be accelerated in a *cycletron*. Hydrogen is not a *mettelloid* nor is it a *transcessional* element.

NEILSSON WILYUM HOOVIE
alias NELSON W. HOVEY

UNIVERSITY OF TOLEDO
TOLEDO, OHIO

To the Editor:

The article "The Rate of Iodination of Aniline" (THIS JOURNAL, **39**, 632 (1962)) contains the statement "these results are consistent with the assumption that I^+ (from $I_2 \rightleftharpoons I^+ + I^-$) is the iodinating species." Although the kinetics are consistent with this view, neither the reactivity of the iodinating species nor the thermodynamic calculations are. Recently a review was published summarizing the considerable body of evidence against iodine cations existing is aqueous media.[1] In this particular instance the mechanism may be

$$H_2O + I_2 \rightleftharpoons H_2OI^+ + I^-$$

with protonated hypoiodous acid as the iodinating agent.

J. AROTSKY

THE HARRIS COLLEGE
PRESTON, ENGLAND

[1] AROTSKY, J., AND SYMONS, M. C. R., *Quart. Rev.*, **16**, 282 (1962).

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Nominations for Officers, 1963–64

Chairman

ROBERT C. BRASTED, Professor of Inorganic Chemistry at Minnesota, also serves as director of the general chemistry program. A native of North Dakota, his training was at George Washington and a PhD from Illinois. After a year in industry, he taught at the University of Hawaii for four years before going to Minnesota. He is well known as an author of text and reference books (Comprehensive Inorganic Chemistry) and has published over 30 research papers. In addition to his extensive consulting to industry, he has held Fulbright and NSF appointments to Germany. He has served the Division on the Visiting Scientist Committee, has directed numerous Summer Institutes, and currently serves on the National Advisory Council on College Chemistry.

CLARK E. BRICKER, Dean of the College of Wooster, will return to full time in the laboratory and classroom in the fall of 1963 at the University of Kansas where he will direct the general chemistry program. A Gettysburg graduate, with a Princeton PhD, he taught at Johns Hopkins before returning to Princeton where he became Professor of Analytical Chemistry. He is co-author of textbooks and an extensive list of research publications, many the work of his undergraduates. A dynamic and enthusiastic teacher, he has lectured widely at NSF Institutes and has directed programs on his own campus. He previously served the Division on the Board of Publications of THIS JOURNAL, as Chairman of the Program Committee, and as a Visiting Scientist.

Councillor

ANNA J. HARRISON is Professor of Chemistry and Chairman of the Department at Mount Holyoke College. After taking her undergraduate and PhD degrees from Missouri, she taught at Sophie Newman College prior to coming to Mount Holyoke in 1946. She has maintained an active interest in photochemical research, having worked at Cambridge University and at the laboratories of the National Research Council of Canada. She has served an extended term as Chairman of the Division's Board of Publications for this Journal. Her sound judgment, broad experience as an outstanding teacher, enthusiasm, and sense of humor have contributed greatly to several of the Division's special conferences and institutes.

WILLIAM H. JONES, Professor of Chemistry at Emory University, is a born Georgia "Colonel" with a PhD from Princeton in reaction kinetics. He has taught general and physical chemistry, done research on molecular structure at Cal Tech and, in addition to work on the Manhattan Project, has spent several summers at Oak Ridge National Laboratory. He has served as President of the Georgia Academy of Science and has been a leader in many programs designed to improve secondary school science education both at NSF institutes on his own campus and in schools throughout the state.

Treasurer

JOHN H. BUCKINGHAM is Professor of Physical Chemistry and Chairman of the Department at Miami University (Ohio). His PhD at Ohio State followed a degree in Chemical Engineering at the South Dakota School of Mines. He has served on Division Committees for Institutes and Conferences. A fourth term councillor for the Cincinnati ACS, he has long service on the Council Committee on Chemical Education as Secretary. He has been Vice President for Chemistry of the Ohio Academy of Science and has been active on committees concerned with teacher training and certification. He has directed Summer Institutes for science teachers and has served on numerous NSF evaluation panels.

WILLIAM G. KESSEL, Professor of Chemistry at Indiana State College, Terre Haute, is completing a three-year term as Treasurer of the Division which has seen the business of the office increase greatly in efficiency as well as magnitude. He has long service with activities of the Division, notably on the former Committee on the Teaching of Chemistry. He has served as a member of the Editorial Board of this Journal, specifically as an editor of the "Basket" section. He has lectured extensively under ACS and Indiana Academy of Sciences auspices on his favorite theme: raising the standards of teacher education and certification.

Ballots will be mailed to members of the Division of Chemical Education and must be returned to the secretary by July 1, 1963. Luke E. Steiner (Oberlin), at present serving as Chairman-elect, will become Chairman; Robert L. Livingston (Purdue) holds the office of Secretary until 1965. Wendell H. Slabaugh (Oregon State) is the Member-at-Large of the Executive Committee.

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Proceedings of the California Association of Chemistry Teachers

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John W. VanLandingham
Bureau of Commercial Fisheries
Washington, D. C.

Inorganic Nutrients in the Sea

In this modern age of space consciousness and sub-space exploration, most of us remain unaware of a less spectacular but equally determined thrust into the inner space of the great oceans and seas covering more than two thirds of the earth's surface. The pressure barrier encountered in this submarine world has been just as effective in limiting man's exploration of the ocean depths as the thermal barrier has been in postponing his direct entry into the fringe areas of interplanetary space, long after he had achieved the rocket capability to do so.

Today the major governments of the world are pouring great sums of money and expending much time and effort into a study of the chemical, physical, and biological properties of the marine environment.

The purpose of the discussion here presented is threefold: to illustrate briefly the practical factors which make such research necessary, to discuss the inter-relationship of the above mentioned properties, and to present a semiquantitative, tridimensional study of the distribution of representative inorganic nutrient materials. The most representative of these nutrients are phosphate-phosphorous and nitrite or nitrate-nitrogen. The scope of this paper will be limited to inorganic phosphate and dissolved oxygen.

Dissolved oxygen is being discussed for three reasons: firstly, it is just as vital to the welfare of the marine organism as are the nutrients; secondly, because it is important to the physical oceanographer in his study of the structure and transport of water masses; and finally, because there is a unique relationship between the distribution of dissolved oxygen and that of the nutrients.

Most people might suppose the oceans to be rather homogenous masses of water in which fish and other organisms are randomly distributed. However, years of chemical, physical, and biological research have shown such conceptions to be erroneous. We now know that the chemical and physical properties of sea water vary considerably with respect to both the horizontal and vertical dimensions of the oceans. Paralleling this variability in the properties of sea water we frequently find a systematic diversification (or in some cases limitation) of the bio-types encountered in any particular environment (*2, 3*).

Since the harvest of the sea is a vital factor in our economy it has become increasingly important to study this problem of nutrient distribution and its relationship to the biological population on an ever expanding scale. Any such study of nutrient distribution must first consider the structure of the oceanic water masses. The most important aspect of this structure involves the vertical profile of the water from the surface to the bottom. This column may be divided into three zones, the uppermost of which is called the euphotic or photosynthetic zone. This is the layer of the water mass in which the intensity of the penetrating sunlight is sufficient to provide the photochemical energy required by the chlorophyll bearing organisms. This zone extends to a depth of 100 or 200 m (*1, 4*) depending upon the clarity of the water and the intensity of the ambient sunlight. The euphotic zone is the most heavily populated region in the water column and is the one which is most seriously affected by climatic conditions at the surface. The predominant life forms in this zone are the phytoplankton and zooplankton, the microscopic plants and animals of the sea.

Far below the euphotic zone lie the abyssal depths where conditions are quite different from those near the surface. Here turbulence and light penetration are practically nil, and abyssal current velocities are almost imperceptible compared to those in the upper layers. Abyssal water is isolated from the sunlit euphotic zone by the midwater region, a zone of gradual but continuous change in physical properties and in nutrient concentration. The mid-water zone is usually preceded by a distinct layer of water which is characterized by rapid changes in its physical properties. The abrupt nature of these changes is responsible for the descriptive name "discontinuity layer" (*5*) which has been applied to this zone. The thickness of the discontinuity layer as well as the depths of its upper and lower boundaries are quite variable. The upper limit frequently reaches well up into the euphotic zone and the lower boundary may extend down to 200 m (*8*). This zone is just as important to the marine community as is the euphotic zone. Many of the larger forms of marine animals appear to prefer the lower temperature beneath the euphotic zone but in many cases will ascend into this region to forage for food (*11*).

Vertical Transport of Water and Nutrients

In Figure 1 we have a schematic representation of the life cycle in the sea; beginning with the nutrient chemicals at the bottom of the chart, progressing upward through the phytoplankton, branching on around

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to include the zooplankton and fish and finally returning again to the nutrient materials to complete the cycle. The nutrient cycle actually begins in the land masses of the earth, and as a rule, in the higher altitudes of these land masses. Here we have heavy rainfall situations predominating, with concurrent leaching of the soluble nutrient materials from the soil which run off, through the streams and rivers, and eventually drain into the sea. This alluvial run-off, by reason of its greater freshness, is less dense than sea water. Therefore it tends to spread out on the surface of the sea and is carried into the open ocean by the prevailing surface currents. When these nutrients come in contact with the marine environment they are eventually consumed by the phytoplankton and assimilated into

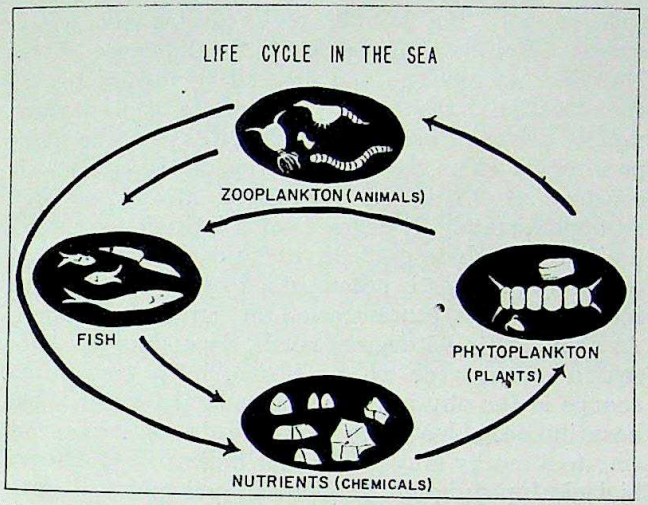


Figure 1. The life cycle in the sea.

their cellular structure. From this point on the chemical nutrients become an integral part of the living food chain. A natural result of the metabolic activity of these organisms is to return a portion of the nutrients to the water in the form of either soluble or particulate organic matter. The particulate matter with its adsorbed ions, together with the skeletal remains of those organisms which are not completely devoured by their predators (*15*), settle downward under the influence of gravity and eventually drop out of the euphotic and discontinuity zones into the quiet waters of the midwater and abyssal depths. During the sedimentation process the particulate matter is attacked by various species of bacteria including those of the chemosynthetic variety. As a result of this bacterial decomposition some of the nutrient materials are regenerated in their soluble inorganic forms. The final stage in this nutrient cycle should then be to return the regenerated material to the euphotic zone where it would again become available for consumption by the phytoplankton.

Such vertical transport of water and nutrient material can take place by several means. Figure 2 illustrates one variety of vertical transport called upwelling. In this particular case a wind blowing parallel to the coast line of a land mass displaces surface water offshore at an angle with the direction of the wind. The viscosity effect of this surface current tends to pull nutrient-rich deep water up the sloping shelf of the land mass and disperse it in the euphotic zone. Another type of upwelling occurs when an abyssal current impinges upon a submarine bank (Fig. 3). On the current side of the shoal abyssal water is deflected up toward the surface and if the banks are high enough and the velocity of the current is great enough this deep water reaches the euphotic zone. Notice also that on the leeward side of the shoal water is pulled upward by an eddy effect. A similar condition occurs when a surface current impinges upon an island mass (Fig. 4). Here, however, the nutrient layer is deflected away from the surface on the current side of the land mass, but again on the leeward is forced upward by an eddy effect.

Vertical water transport sometimes occurs far from the influence of land masses or sea mounts. Such a situation develops when a warm tropical water mass converges with one of significantly lower temperature. Here the thermal difference between the two water masses creates a great deal of vertical turbulence and mixing all along the points of juncture (*9*). The several zones of diffusion are represented in Figure 5 by the varicolored bands. Another mechanism for vertical transport of nutrients is called vertical eddy diffusion (*6*). This is a cyclical phenomenon produced by wave action on the surface which creates a series of

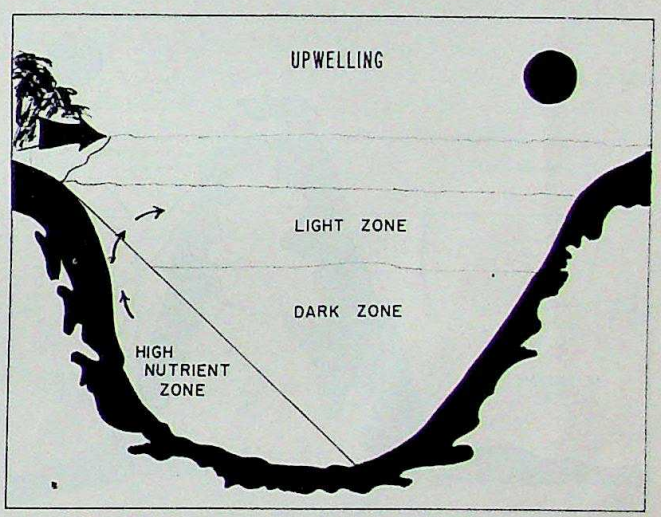


Figure 2. Upwelling produced by wind and surface current in the vicinity of large land masses.

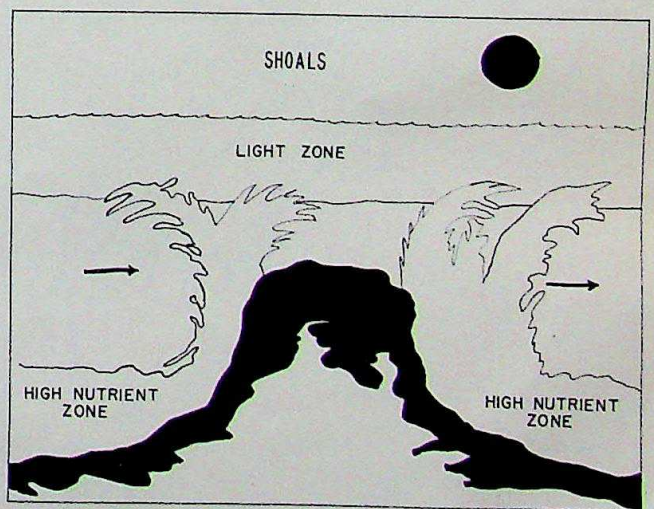


Figure 3. Upwelling produced by a sub-surface current impinging upon a submarine bank.

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vertical eddies along the water column. The oscillatory motion of the water in these eddies increases the rate of diffusion of nutrient water upward against the force of gravity. However, this process is not nearly as effective as upwelling. A similar cyclical pattern of circulation is produced by convection cells (*10*). These cells are formed by convection currents arising from a negative thermal gradient, or temperature inversion, where a warm water mass is occluded within or beneath a cold water mass.

Any condition which inhibits this vertical movement of water is called stability (*5*). Such a condition is caused by a positive density gradient (i.e., a rapid increase in density with depth). The density gradient, in turn, is related to either a rapid decrease in temperature with depth, or a rapid increase in salinity, or in some cases a combination of these two effects. However, since this phenomenon is usually associated with a thermal gradient we call it the thermocline or discontinuity layer. Since large expanses of the ocean areas have a reasonably well developed thermocline either briefly during the warm summer season in temperature zones, or throughout the year in tropical regions, vertical transport is effectively retarded in most of the oceanic areas. The net effect then, is depletion of the nutrients by biological utilization in the euphotic zone of these areas and regeneration and accumulation of nutrients in the abyssal regions.

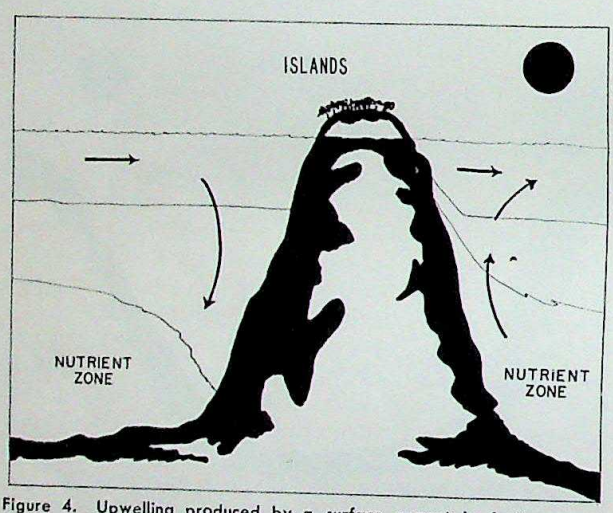


Figure 4. Upwelling produced by a surface current impinging on an island mass.

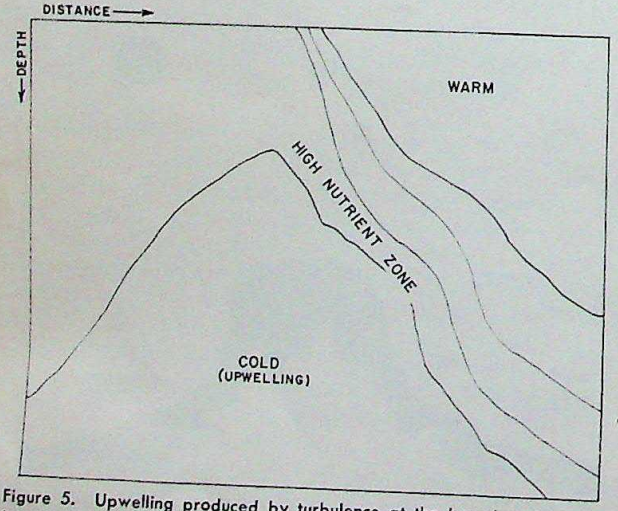


Figure 5. Upwelling produced by turbulence at the boundary between two water masses.

Surface Distribution of Inorganic Phosphates

Let us now examine the distribution of inorganic phosphate in the surface waters along the north-south plane of the Pacific Ocean. In theory we will take an oceanographic cruise from the equator to the Aleutian Islands, beginning the expedition in our own island paradise of Hawaii, which lies at approximately 20 degrees north latitude. In the vicinity of Hawaii, in the immediate inshore and offshore waters, the island mass effect which has been discussed earlier is in operation. Phosphate values are generally higher and subject to fluctuations, the peaks of which usually coincide with the rainfall peaks during the winter season. However, as we leave the influence of the Hawaiian Archipelago and proceed northward toward the Aleutians, the surface phosphate concentration rapidly decreases and we find ourselves in a phosphate poor region where the concentration remains relatively constant at 0.1 to 0.3 microgram atoms per liter. At approximately 30 degrees north latitude we enter a positive phosphate gradient where each change in our northerly progress is accompanied by a corresponding increase in the concentration of surface phosphate. At about 30 to 45 degrees north, depending upon the season of the year we are struck by a tremendous change in the physical appearance of the water. The beautiful deep blue of the sub-tropical regions has given way to a murky gray-green color indicative of a heavy biological population. Chemical and physical analysis of the water reveals drastic changes in these properties. Phosphate has increased until it is now ranging from 1 to 1.5 microgram atoms per liter. Oxygen has increased and salinity has decreased. The temperature of the water is quite variable but generally much colder. There are several factors responsible for this remarkable change in the ocean water. One is the fact that we have crossed a front between two distinct water masses. Here the cold subarctic water mass converges with the warmer subtropical waters of the central Pacific. In addition we are now in a temperature zone where thermocline development weakens at the end of the summer season and is almost completely broken down by the storms that prevail in the area during the fall and winter season (*7*).

If we proceed due south from Hawaii to the equator we find that the phosphate poor region extends as far south as 5 degrees north latitude. As we pass 10 degrees north latitude we enter one of the strange marine desert areas which border the equatorial zone. Here the surface phosphate concentration is very low and the water itself appears to be almost completely devoid of plant or animal life. This paucity of marine life in the surface water is reflected in the chemistry of the bottom sediments.

Continuing on toward the equator, at about 5 degrees north latitude we again enter a positive phosphate gradient. And then in the neighborhood of 3 degrees north we again find all of the visual and analytical evidence of strong upwelling of nutrient rich water and its highly productive biological population.

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This should come as a surprise, because in this torrid tropical zone we could reasonably expect to find a well-developed thermocline existing throughout the year. However, other factors have entered into the picture. As a result of the combined effects of the trade winds and the rotation of the earth upon its axis, the action and reaction of the current systems from both hemispheres come to a focus along the equatorial belt. The interplay of these hemispheric forces promotes the upwelling of deep nutrient rich water into the euphotic zone.

We should keep in mind that we have been discussing the typical pattern of the distribution of surface phosphate in the Pacific Ocean and that there are frequently temporary and localized deviations from this pattern. For example, ships often pass through patches of discolored water which are called "plankton blooms." These blooms may reflect an unexpected and oftentimes inexplicable enrichment of the surface water. They are often followed by a depletion of the nutrient responsible and a subsequent disappearance of the phenomenon.

From these observations we see that the surface concentration of inorganic phosphate is primarily determined by two factors—the rate of biological consumption and the rate of physical replenishment. Note also that phosphate concentration may be a limiting factor regulating the size of the bio-mass. Let us now examine the distribution of surface oxygen in these same waters.

Surface Distribution of Oxygen

Normally all surface water is supersaturated with oxygen as a result of wind and wave turbulence at the air-water interface, often in combination with a diurnal photosynthetic enrichment. The surface oxygen concentration is at a minimal value in the tropical waters of the equatorial belt. Each change in northerly progress from this boundary is associated with a corresponding increase in the concentration of surface oxygen. In the latitudes of Hawaii the concentration value is approximately 5 ml per liter, and we will notice that there is no predictable difference between the concentrations in inshore and extreme offshore waters as we had in the case of phosphate. We now know that the concentration of dissolved oxygen on the surface is affected by many more variables than phosphate. For example, oxygen values are a result of the interaction of biological consumption, biological production, turbulence, temperature, and salinity (*14*). Surface oxygen is not normally a limiting factor to biological growth as is frequently the case with phosphate. However, there are rough correlations between oxygen and phosphate concentrations on the surface as well as at specific points down the water column. For example, a heavy phytoplankton bloom resulting from phosphate enrichment will probably be associated with a significant increase in the degree of supersaturation.

Vertical Distribution of Nutrients

In Figure 6 we have vertical profiles of the oxygen and phosphate concentration plotted against the depth in meters. We note the general inverse relationship between the concentrations of the two substances. An increase in phosphate is associated with a decrease in oxygen, and the prominent features of one curve are replicated on the other although not necessarily at exactly the same depth. Observing the oxygen curve in detail, we note that the concentration is a high 5 ml per liter at the surface but increases to a maximum at about 50 m. From this point downward a gradual but continuous depletion of oxygen is observed which is markedly accelerated at a depth of 500 m. Finally, at 1200 m a minimal value is reached beyond which the concentration gradually increases. Extrapolation of this curve would show the oxygen concentration increasing in the deep abyssal waters until it might equal or exceed the surface value.

Phosphate on the other hand is a low 0.2 microgram atoms per liter on the surface and diminishes even further immediately below. Beneath this point the concentration increases in direct opposition to that of oxygen until the abyssal maximum is reached. Extrapolation of the phosphate curve would show relatively small fluctuations about this maximal value.

The most interesting portions of these profiles are the significant maxima and minima occurring in both the euphotic zone and the upper abyssal zone. These features are commonly found in many oceanic water masses. At one time these apparent anomalies were a complete mystery. However, we can now definitely explain the euphotic zone anomalies and even reproduce them on a laboratory scale. It seems that ultraviolet light has a detrimental effect on the photosynthetic process, and in the uppermost layer of the water the intensity of ultraviolet radiation is great enough to

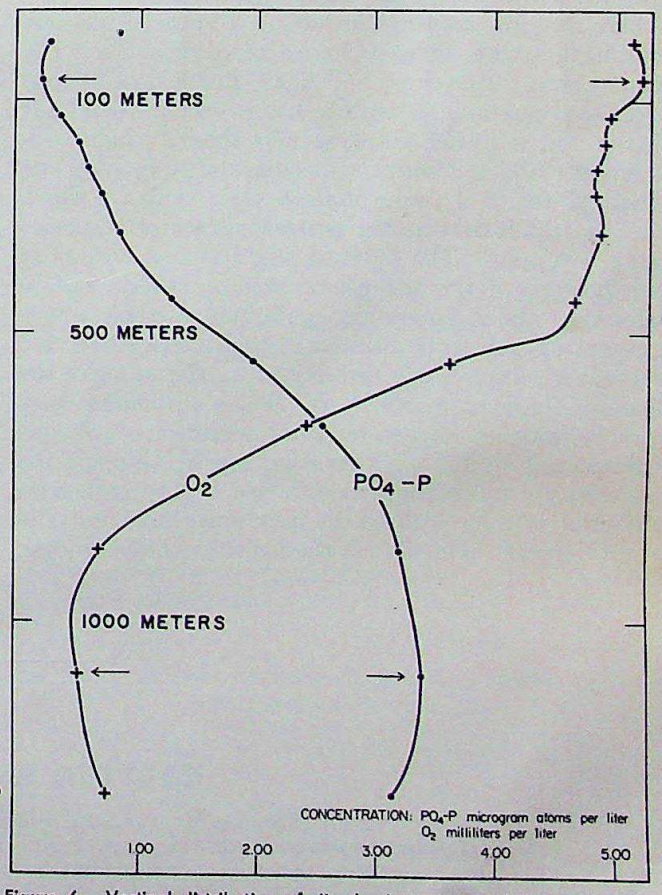


Figure 6. Vertical distribution of dissolved oxygen and inorganic phosphate in a typical Pacific Ocean water column.

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inhibit this process. After traversing just a few meters of the water column this radiation is reduced to the point that photosynthesis proceeds at its maximum rate, thus accounting for the sub-surface phosphate minimum and oxygen maximum.

The abyssal phenomenon is not as readily explained. It is indirectly related to biological activity, but may also be associated with a physical factor. Application of the principles of physics indicates that whenever a water mass is flowing over and in opposition to another mass, vertical exchange between the two water masses is facilitated and if the oxygen renewal exceeds the consumption rate in one mass (and it does) then minimum oxygen values could be expected to coincide with the current boundary. The mathematicians have come to the assistance of the oceanographer and evolved a system of equations to support this theory (*12*).

We should now consider the phenomenon of oxygen enrichment in abyssal waters. Oxygen concentration in surface waters is highest in the frigid polar regions of the earth's hydrosphere, reaching values in excess of 10 ml per liter. Some of this polar water will inevitably converge on warmer water masses from lower latitudes. As a result of the greater density of this extremely cold water it will tend to sink down through the warmer layers into the abyssal depths, carrying along its rich supply of dissolved oxygen. Since biological activity is limited at these extreme depths the oxygen concentration remains high. Now there is no doubt but that this process is continuously taking place and extracting oxygen from the polar atmosphere and transporting it down into the depths of the sea. The obvious conclusion resulting from this knowledge is that the hydrosphere and the atmosphere are in a state of gaseous equilibrium, the primary source of oxygen being the atmosphere. However, Dr. A. C. Redfield of Woods Hole Oceanographic Institute has in recent years (*13*) introduced a rather startling new theory which considers the above described phenomenon to be only one small phase of a tremendous oxygen cycle in which the sea itself is the primary generator of our atmospheric oxygen supply. The point of origin of this cycle is at the bottom of the sea where chemosynthetic sulfate bacteria, under anaerobic conditions are extracting nascent oxygen to be utilized in their metabolism and returning soluble combined oxygen to the water in the form of inorganic carbonates. These carbonates provide an immense oxygen reservoir, a portion of which is transported to the photosynthetic zone through the processes of upwelling and diffusion. The carbonate material is then utilized by phytoplankton and elemental oxygen released via the photosynthetic process. Diffusion of the oxygen into the atmosphere and back again now proceeds in accordance with the principles of chemical and physical equilibria.

Another phenomenon may affect the oxygen concentration in the abyssal regions. Whenever abyssal water masses are trapped within deep oceanic basins, as in the Black Sea, deep circulation may be completely stopped. Under these conditions the dissolved oxygen supply may be quantitatively depleted, followed by the establishment of anaerobic biological population. Significant concentrations of dissolved hydrogen sulfide will then appear in the water column in lieu of the normal oxygen supply.

Summary

We have examined some of the most important mechanisms involved in the vertical transport of water. We have studied geographical and vertical distributions of some representative nutrient materials in one of our principal ocean areas, and finally we have considered the relationship between the concentrations of these substances and the biological productivity of any given water mass. All of these items are dynamic variables in the gross aspect of the earth's hydrosphere, and their quantitative values fluctuate in response to both random and periodic changes in the total environment.

Acknowledgments

The photographs from which the illustrations were made were produced by members of the Thai Royal Navy Hydrographic Office in cooperation with Dr. E. C. La Fond. Copies were made available for this paper through the courtesy of Mr. James L. Faughn, Project Leader of Expedition Naga.

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CACT Fifth Summer Conference

Dates: August 18 evening through noon August 24.
Location: Asilomar Beach State Park, Pacific Grove, Calif. See April 1963 issue of this Journal, page 222, for details of program featuring outstanding chemists.
For Information Write: Mrs. Wallace A. Craig, CACT Conference Coordinator, 1199 Laurel St., Pasadena, Calif.; or Dr. Frank L. Lambert, CACT President, Occidental College, Los Angeles.

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Report of the **New England Association of Chemistry Teachers**

Roland Ward
University of Connecticut
Storrs

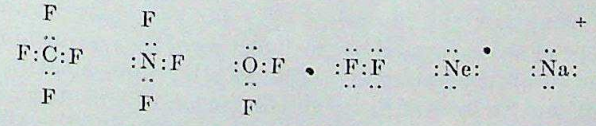
Would Mendeleev Have Predicted the Existence of XeF_4?

The astonishment with which most of us inorganic chemists received the news of the isolation of xenon tetrafluoride (*1*) marked the event as a first rank accomplishment of the practical chemist. The preparation of this compound and other fluorides of the noble gases has been carried out in many laboratories in recent months. Some of them have been found to be remarkably stable.

When one recovers from the first surprise of these events, a vague feeling of guilt begins to grow in one's consciousness. Should one have suspected the existence of such compounds? Would a present day Mendeleev—indoctrinated with the notions of electronic orbitals—have been able to predict the existence and shape of these molecules? I think the answer is yes!

We have been accustomed to thinking of the periods of the periodic table beginning with group I and ending with the inert gas group. Our freshmen have been taught that the atoms of the noble gases are inert because the eight outer electrons form a stable group. This seems to bring the period to a definite end in a neat and logical way.

We list the fluorides of the elements in which the central atoms can be regarded as having eight electrons (forming tetrahedral molecules including unshared electron pairs) using sp^3 hybrid orbitals. The compound OF_2, for example, could be regarded as a tetrahedral molecule as illustrated in Figure 1 (the angle F-O-F is 103.2°).



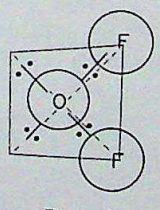


Figure 1

This leads us directly to neon and the sodium ion and it seems convincing that they are "happy" with eight electrons. Should we pursue this idea, however, in the subsequent periods, we find a widening gap in the sequences as shown in Table 1.

SF_2 has been reported (*2*) but not substantiated. BrF is unstable with respect to the reaction:

$$3\ BrF \rightarrow Br_2 + BrF_3$$

The inference might be made that the eight electron configuration is not very attractive for selenium, tellurium, or iodine and possibly not for xenon and radon.

Let us now consider the sequences of fluorine compounds with the central atom sharing ten electrons—presumably using sp^3d orbitals and having the trigonal bipyramid orientation of ligands like the planar chlorine trifluoride molecule (Figure 2). A list of these is given in Table 2.

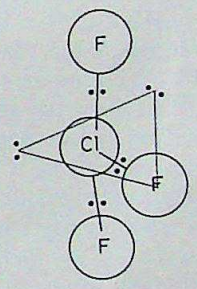


Figure 2

Table 1. Octet Compounds, Atoms and Ions

SiF_4	PF_3	(SF_2)	ClF	Ar	K^+
GeF_4	AsF_3	...	$\underline{BrF}^a$	Kr	Rb^+
SnF_4	SbF_3	...		Xe	Cs^+
PbF_4	...	...	...	Rn	Fr^+

[a] The compounds underlined are "unstable."

The compounds in the square brackets are, of course, ionic but their boiling points are not very high and they do exist in the gas phase as MF molecules. The boiling

Table 2. Fluorine Compounds with Ten Electrons around the Central Atom

PF_5	SF_4	ClF_3	$\{ArF_2\}$[c]	[KF][b]
AsF_5	SeF_4	BrF_3	$\{KrF_2\}$	[RbF]
SbF_5	TeF_4	$\underline{IF_3}^a$	$\{XeF_2\}$	[CsF]
BiF_5	(PoF_4)			[FrF]

[a] The compounds underlined are "unstable."
[b] The compounds in square brackets are ionic.
[c] These compounds are in braces because of a not overpowering temptation.

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point of cesium fluoride is 1250°C. What is the nature of the bonding in these molecules? IF_3 is very unstable and decomposes rapidly to I_2 and IF_5 (*3*). One might be tempted to add ArF_2, KrF_2, and XeF_2, but the temptation at this stage is not very overpowering.

We proceed now to the octahedral configurations, the central atom of which is presumably using sp^3d^2 orbitals such as bromine pentafluoride (Figure 3). Table 3 shows some ions and molecules with this configuration.

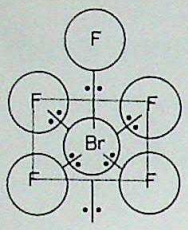


Figure 3

Table 3. Ions and Molecules with Twelve Electrons per Central Atom

SiF_6^{-2}	PF_6^{-1}	SF_6	ClF_4^-	
GeF_6^{-2}	AsF_6^{-1}	SeF_5^{-1}	BrF_4^-	
		SeF_6	BrF_5	KrF_4
SnF_6^{-2}	SbF_6^{-1}	TeF_6	IF_5	XeF_4

The formation of RbF_3 and CsF_3 has been reported (*4*) to occur by the reaction of fluorine on the chlorides, bromides, or iodides of rubidium and cesium. It has been shown, however, that the interpretation of the experimental data was wrong and that the reaction yields fluorohalates MXF_4 (*5*). The tetrafluorochlorate(III) ion is much less stable than the corresponding bromine compound. The tendency towards octahedral configuration seems to increase in periods 4 and 5. Hence the extrapolation to the octahedral compounds KrF_4 and XeF_4 seems reasonable.

The well-known "diagonal relationship" in the periodic table is represented by the trigonal bipyramid sequence:

SF_4 BrF_3 XeF_2

and by the octahedral sequences:

	ClF_4^-	KrF_4(*6*)
SF_6	BrF_4^-	XeF_4
	BrF_5	

The known inert gas fluorides do not seem out of place in these lists.

Further expansion of the valence shell of electrons is not common. The pentagonal bipyramid molecule

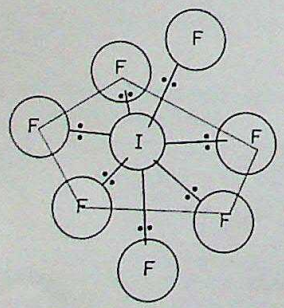


Figure 4

IF_7, Figure 4, is the only established case in this part of the periodic table (*7*). The structure of the IF_7 molecule as it occurs in the orthorhombic form (*8*) could be described as a distorted pentagonal bipyramid, two of the equatorial fluorines being at a larger distance from the iodine than the other five. Some Lewis acid character has been found, however, in the compound TeF_6 (*9*). Muetterties has suggested TeF_7^- and TeF_8^{-2} as possible formulae for the complex ion in the compounds of composition 2 MF·TeF_6. Compounds of the type M'_2SeF_6 are listed without reference by Heslop and Robinson (*10*). Perhaps the lateral sequence and the diagonal sequences may be suggested.

SeF_6^{-2}

TeF_7^{-1} IF_7 {XeF_6}

{RnF_6}

One would predict the existence of RnF_6. This structure would be like that of IF_7 with one of the equatorial fluorines removed.

Another parallel that suggests itself is a comparison of the halogen fluorides and inert gas fluorides given in Table 4. The underlined compounds among the interhalogens are unstable. Corresponding to the stable

Table 4. Comparison of Halogen Fluorides and Noble Gas Fluorides

Tetrahedral	Trigonal bipyramidal	Octahedral	Pentagonal bipyramidal
ClF	ClF_3		
BrF[a]	BrF_3	BrF_5	
	IF_3	IF_5	IF_7
Ar	ArF_2		
Kr	KrF_2	KrF_4	
Xe	XeF_2	XeF_4	XeF_6
Rn	RnF_2	RnF_4	RnF_6

[a] The compounds underlined are "unstable."

ClF and ClF_3 we would expect only ArF_2. Following on the stable BrF_3 and BrF_5 there should be KrF_2 and KrF_4. One would predict that RnF_2 would be very unstable and that RnF_4 and RnF_6 should exist. XeF_2 is known to be unstable. The existence of XeF_6 has been established.

The chemistry of an element is enlarged beyond all measure in its ternary compounds. How about the possibility of the existence of complex cations or anions of the inert gas fluorides? By far the most common type of anion formed by the fluorides of the non-metals is the octahedral complex. The fourth group elements Si, Ge, and Sn form XF_6^{-2}; the fifth group elements P, As, Sb, in the pentavalent state give XF_6^{-1}. Trivalent antimony yields SbF_5^{-2}, an octahedral ion (*11*). In the compound $KSbF_4$, the anion is not of the trigonal bipyramid type but is a complex $Sb_4F_{16}^{-4}$ formed by a ring of four octahedral-type units sharing two corner fluorides (*12*). PF_3 is absorbed by CsF and KF at 150°C but undergoes disproportionation to give MPF_6 and red phosphorus. The PF_4^{-1} ion, if formed as an intermediate, is very unstable (*13*). In the sixth group, selenium gives the compounds $MSeF_5$ (with M = alkali metal). SeF_5^{-1} is most likely an octahedral type. BrF_3 readily yields the octahedral ion BrF_4^{-1} in which all the fluorines are in equatorial positions. The trigonal bipyramid type of anion so common among the XYZ^{-1} linear

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anions does not seem to be represented by any XF_2 species. The evidence for the existence of AsF_4^{-1} is not clear (*14*). There are not many fluoro cations but there is convincing evidence for the existence of the tetrahedral cations BrF_2^+ and SF_3^+, by the reaction of BrF_3 and SF_4 with powerful fluoro Lewis acids. Similar evidence points to IF_4^+ which should be of the trigonal bipyramid type.

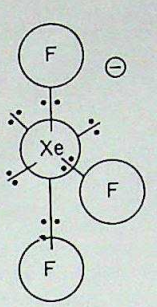


Figure 5

The best bet for a fluoro anion of the inert gases would therefore appear to be an octahedral-type anion. A possible candidate for this would be XeF_2 which might yield the ion XeF_3^-, (Figure 5); and if I were Mendeleev, this is where I would stop.

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NEACT Twenty-Fifth Summer Conference

August 19–24, 1963

University of New Hampshire, Durham

Monday, August 19
7:30 P.M. "The Flash of Genius," Dr. Alfred B. Garrett, Ohio State

Tuesday, August 20
9:00 A.M. "The Unique Element," Dr. John E. Cavelti, Allegheny
"Experimental Aspects of Thin Layer Chromatography," Dr. James M. Bobbitt, University of Connecticut
2:00 P.M. "Rare Earths," Dr. Clement J. Rodden, New Brunswick Laboratory, Atomic Energy Commission
"Oxide Systems of the Transition Metals," Dr. Roland Ward, University of Connecticut
7:30 P.M. "The Role of Agricultural Chemicals in Feeding an Exploding Population," Dr. Robert H. White-Stevens, American Cyanamid

Wednesday, August 21
9:00 A.M. "Design of Experiments," Dr. Arnold J. Rosenthal, Celanese Corporation of America

Thursday, August 22
9:00 A.M. "Advance Studies in Science and Mathematics for Secondary Students," Mr. Clair G. Wood, Thayer Academy
"Chemical Education in the Soviet Union on all Levels," Mr. George Siemiencow
2:00 P.M. "Institute Programs of the National Science Foundation," Dr. Harold A. Iddles, National Science Foundation
"Structural Chemistry of Silicates," Dr. Donald W. Breck, Linde Company, Union Carbide Corporation
7:30 P.M. "Chemistry in Relation to Mental Illness," Dr. John R. Bergen, Worchester Foundation for Experimental Biology

Friday, August 23
Dr. William F. Kieffer, Journal of Chemical Education
Dr. Calvin A. VanderWerf, University of Kansas
Dr. Edward L. Haenisch, Wabash College

This series of meetings will complete a quarter of a century of summer conferences for the New England Association of Chemistry Teachers. In addition to the program the usual family activities and social events have been planned. More complete details about the program, together with registration forms, are available from Dr. Dorothy W. Gifford, Lincoln School, Providence, Rhode Island.

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Chem Ed

BOOK REVIEWS

Reactions of Organic Compounds: A Textbook for the Advanced Student

Reynold C. Fuson, University of Illinois, Urbana. John Wiley and Sons, Inc., New York, 1962. viii + 765 pp. 16 × 23.5 cm. $12.95.

This book is essentially a revision and updating of the previous volume, "Advanced Organic Chemistry," published in 1950 and reviewed in J. CHEM. EDUC., 28, 664 (1961). The organization of the material has been considerably altered from the functional group approach of the earlier book to a classification under the three general headings of polar, radical, and molecular reactions. Within the part on polar reactions a division is made on the basis of consideration of the reagent as electrophilic or nucleophilic.

Electrophilic reactions covered include the usual substitutions of aromatic compounds including simple heterocyclic and activated benzenoid compounds "having sensitive nuclei," Friedel-Crafts ring closure, and appropriate reactions of unsaturated aliphatics. Molecular rearrangements involving electron deficient carbon atoms, those involving nitrogen or oxygen atoms, and oxidations with agents such as dichromate and permanganate which probably do not operate by one-electron transfer mechanisms serve as a transition to reactions which are commonly thought of as nucleophilic. Types of the latter discussed are displacement reactions at saturated carbon, at aliphatic trigonal carbon, and in the aromatic series. Also included are elimination reactions, addition reactions of unsaturated compounds, reactions of organometallic compounds, reactions of carbonyl compounds with enolates and phenolates, and nitrogen analogs of carbonyl compounds. Reductions by dissolving metals, aluminum alkoxides, metal hydrides and a number of other reagents are classed as nucleophilic.

The first chapter on radical reactions presents brief consideration of their formation, stability, and reactivity and then gives examples of bimolecular reduction, the Hunsdiecker, Sandmeyer, Meerwein, and Kolbe reactions, aromatic substitution, polymerization, etc. Separate chapters are devoted to aliphatic radical substitutions, reactions of organic halogen compounds with metals, and catalytic reactions involving hydrogen. Thermal decarbonylation and decarboxylation are classed as radical processes.

The portion dealing with molecular reactions includes the Cope and related rearrangements, ester pyrolysis, 1,3-dipolar additions, the addition of carbenes to olefins, and cyclo-additions involving benzyne, as well as the Claisen, Chugaev, Diels-Alder, and other older examples.

The theoretical material given in the preface and accompanying the discussion of a number of the reaction types seldom exceeds, and in a number of instances falls short of that given today in a good one year elementary course. Therefore the book cannot be recommended to the advanced or even intermediate student for its theoretical content. Its chief value to the undergraduate or graduate student would seem to be in aiding the student to organize his knowledge of reactions qualitatively in terms of general reaction types and in providing a good selection of useful additional examples. The book could serve also as a preliminary reference for the chemist who is faced with a particular preparation or transformation and wishes a quick check on the feasibility of alternative methods.

There are some instances of less than careful writing, particularly in the theoretical portions, and a few formulas which are distorted or poorly printed but the accuracy, type, and appearance are in general good. The subject index is adequate.

No one text can fill the needs of the advanced student of organic chemistry. The separate aspects of the subject each require one or more books written by authorities who are specialists. The present text is a largely descriptive presentation of the more important reactions of a good selection of organic compounds by one who knows this aspect very well. Another recent book of this type is "Advanced Organic Chemistry" by L. F. Fieser and M. Fieser, and the prospective buyer would do well to consider both books before making his purchase.

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Structural Inorganic Chemistry

A. F. Wells. 3rd ed. Oxford University Press, at the Clarendon Press, 1962. xxvi + 1055 pp. Figs. and tables. 16.5 × 24 cm. $10.

One of the central problems in the chemistry of solids is the prediction of possible crystal structures for a given stoichiometry. No one has analyzed this problem in topology as has A. F. Wells. Just as the previous editions of "Structural Inorganic Chemistry" were well received (see J. CHEM. EDUC., 28, 502 (1951)), this edition deserves a place on bookshelves, provided that they can support a volume of this size. The growth of the field is well documented by the increase in pages from 590 in the 1945 edition to 709 in 1950, and 1028 in the present volume. The expansion makes this edition more of an encyclopedia than a text and the price is probably out of reach of many students. Serious consideration should be given to producing a textbook version based on the principles in the first part of the book.

Considerable attention has gone into each section. Even in many areas where it has not been necessary to include new references, the text has been rewritten for greater clarity. Charts and graphs have been brought up to date. It is difficult to find sections in the second edition which have been taken over unchanged. Some of the more important additions are sections on Ligand Field Theory, *n*-connected nets and the packing of polyhedra, and resonance spectroscopy techniques in structure analysis. The enlarged treatment has resulted in the following new chapters: Complex Oxides, The Elements

Reviewed in This Issue

Reynold C. Fuson, Reactions of Organic Compounds: A Textbook for the Advanced student
A. F. Wells, Structural Inorganic Chemistry
J. M. Wilson, R. J. Newcombe, A. R. Denaro, and *R. M. W. Rickett*, Experiments in Physical Chemistry
Alvin Glassner, Introduction to Nuclear Science
Aleksander Abramovich Grinberg, An Introduction to the Chemistry of Complex Compounds
F. Albert Cotton, editor, Progress in Inorganic Chemistry. Volume 3
Roy L. Whistler and *M. L. Wolfrom*, editors, Methods in Carbohydrate Chemistry. Volume 1, Analysis and Preparation of Sugars
W. A. Smeaton, Fourcroy: Chemist and Revolutionary
Eduard Farber, Great Chemists
N. A. Figurovskij, Leben und Werk des Chemikers Tobias Lowitz: 1757-1804
W. B. Renfrow and *P. J. Hawkins*, Organic Chemistry Laboratory Operations
Adolphe Chapiro, editor, High Polymers. Volume 15, Radiation Chemistry of Polymeric Systems
Farrington Daniels, J. W. Williams, Paul Bender, Robert A. Alberty, and *C. D. Cornwell*, Experimental Physical Chemistry
Andrew Streitwieser, Jr., Solvolytic Displacement Reactions

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of the VA and VB Subgroups, Other Elements, and The Inert Pair. Subgroup Elements, and The Inert Pair.

Chapter III, The Geometrical Basis of Crystal Chemistry, is a revision of Well's review article in *Solid State Physics*, **7**, 426 (1958), which represents a bridge between the second and third editions of "Structural Inorganic Chemistry."

The Formula and Subject Indexes only give reference to the major discussions. Further page references are given there to related material in the text, but the reader will find tidbits in unexpected places along the way.

The reviewer cannot claim to have read every page in detail (it being desirable to review this book before the fourth edition appears), but there appear to be no technical or typographical blemishes.

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Experiments in Physical Chemistry

J. M. Wilson, R. J. Newcombe, A. R. Denaro, and *R. M. W. Rickett,* College of Technology, Liverpool, England. Pergamon Press, Ltd., Oxford, 1962. xii + 290 pp. Figs. and tables. 15.5 × 23.5 cm. $4.50.

This physical chemistry laboratory manual was written at one of the newer British technical colleges by a group of authors including at least one (R. M. W. Rickett) who received his entire graduate training in the USA. The result of their effort is a manual which is eminently suitable for use in many American undergraduate physical chemistry laboratories. In many ways this book bridges the gap between the two types of manuals which have evolved in this country: the short, limited-content text which does not touch at all upon recent advances in physical chemistry, and the manual which in order to remain contemporary contains increasing numbers of experiments requiring equipment out of reach for smaller departments.

The book contains just over 100 experiments. The first 50 are in the general areas of physical properties and molecular structure, thermodynamics, phase equilibria, light and spectra, chemical kinetics, surface chemistry and colloids, conductance and transference, and electrode potentials and processes. These experiments are the simple, most conventional ones, and their analogs can be found in any representative American text. The second section contains an additional 44 experiments which are in the same areas as those given above, with the addition of 2 experiments in radiochemistry. These experiments are either more difficult to perform or require a more complete theoretical background than the earlier ones. The last section contains 8 experiments which are described as being open-end investigations. However, most of them are really only extensions of earlier experiments and could as well have been treated as "suggestions for further experiment."

One reason for the large number of experiments in the text is that a number are included which could not be performed in other courses in this country. But this diversity of experiments, crossing the conventional boundaries of chemistry, makes this book refreshingly different.

Even within the realm of what would universally be considered physical chemistry, there are significant differences in emphasis. For example, in addition to the usual experiments involving spectrophotometry in the visible region, this text includes some relatively simple but enlightening experiments on the effects of molecular structure on UV and IR spectra.

The equipment required for most of the experiments is quite simple. Where specialized electronic or optical equipment is called for, reference is made to units of British manufacture. This is not crucial since the descriptions of the actual operations to be carried out for each experiment are necessarily brief and general.

Practically complete responsibility is placed upon the student so far as deciding what data are required and what form any report should take is concerned.

The book is written in a simple clear style and is free of major typographical errors. It is sturdily bound and attractively printed.

The book does have two obvious shortcomings. Because the text can provide only an abbreviated development of the equations or precedures to be used in each experiment the student is admonished by the authors to read other, more complete discussions. However, in too many instances no key references are given.

The other and perhaps more important omission is a chapter on the treatment of errors. Although the authors assert that "the subject could not be dealt with in sufficient detail within the terms of reference of this book" and the student is instructed to consult standard references in the field, none are even listed.

Even recognizing the shortcomings of this book, the fact remains that it is a good one. Perhaps its greatest asset is that it was written in another country by authors with different preconceived notions as to what constitutes a good choice in physical chemistry experiments.

Any teacher interested in physical chemistry laboratory manuals should be sure to look at this one.

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Introduction to Nuclear Science

Alvin Glassner, Argonne National Laboratory, Lemont, Illinois. D. Van Nostrand Co., Inc., 1961. x + 213 pp. Figs. and tables. 16 × 23.5 cm. $3.75.

The rather special origin of this book has determined its scope and style. In the summer of 1956 and again in the summer of 1957 members of the staff of Argonne National Laboratory organized and presented a short course covering "the field of nuclear sciences" and "parts of the natural sciences touching on that field" for high school teachers. The purpose of the course was twofold: "to survey the field, highlighting recent developments"; and "to emphasize the experimental and laboratory aspects of science." Altogether 56 members of the Argonne staff participated in the courses; and the present book is based on their lectures. Dr. Glassner acknowledges his indebtedness to the Argonne "teachers" very gracefully: "Without them this book would not have been written. Their lectures have been 'plagiarized' and their experiments have been reprinted. Theirs should really be the credit." Dr. Glassner himself is to be credited with producing an excellent book which should be of value not only to high school teachers, but also to college teachers and college students who have need of a well-written and authoritative survey of the important field of nuclear science.

The volume under review summarizes the material usually presented in textbooks on radiochemistry. Chapter II, for example, presents a good but brief account of the methods commonly employed for the detection of radiation; and Chapter IV gives an adequate exposition of the decay law including even a brief discussion of radioactive equilibrium. In the opinion of the reviewer the author has been especially successful with Chapter V on The Nucleus which deals with such difficult topics as: nuclear spin; nuclear magnetic moments; higher moments; parity; nuclear energy levels; nuclear forces; etc. In addition to the material generally covered in introductory texts this volume (reflecting its origin) has chapters on: (IX) Metallurgy of Uranium; (X) Processing of Reactor Fuels; (XI) The Effects of Radiations Upon Materials; and (XII) Biology and Radiation. Dr. Glassner's volume serves also as an introduction to material not readily available at the introductory level. For example, in Chapter VI on The Reactions of Nuclei there is an interesting section on the synthesis of the elements; and in (XII) the author sketches the relationship between radiation and genetics.

Concerning the laboratory part of the original course Dr. Glassner, in his preface, makes the following comment: "The hope was that, upon returning to their schools, teachers would be able to duplicate and illustrate in their classrooms some fundamental phenomena and principles. Demonstrations and experiments were therefore to be stripped, so far as possible, of expensive instrumentation." The last 20 pages are given over to descriptions of about 20 laboratory experiments. Although this material is an interesting record of the experiments with which the high school teachers became acquainted, it is clear that a number of them are for the record only and cannot be duplicated in the typical high school. Thus, five of the 20 experiments are metallurgy experiments which were designed to give the teacher participants an opportunity to make a fuel element of the type used in the MTR Reactor at Arco, Idaho; and three of them require radiation or other equipment not generally available in high schools. Of the remaining 12 experiments which could be useful classroom experiments only half of them require radio-

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isotopes of any kind. It is of interest to note the classification of these 12 experiments according to the nature of the principles which they are intended to demonstrate or illustrate: radioactive—4; biological—2; and chemical—6. In the latter group are the following experiments: Uranyl Oxalate Actinometer; Liquid-Liquid Extraction Separation; Coprecipitation Experiment; Ion Exchange Separation; Determination of the Solubility of Silver Iodide; and Experiment on Isotopic Exchange. Only the last three of these experiments involve radioactive tracers. All six of these experiments have merit and could be helpful to teachers; the actinometer experiment, which is not generally described in elementary texts, could be useful to both high school and college teachers.

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An Introduction to the Chemistry of Complex Compounds

Aleksander Abramovich Grinberg, Lensovet Institute of Technology, Leningrad, USSR. Translated from the 2nd ed. by *J. Rovtar Leach*. Edited by *D. H. Busch*, Ohio State University, Columbus, and *R. F. Trimble, Jr.*, Southern Illinois University, Carbondale. Addison-Wesley Publishing Co., Inc., Reading, Massachusetts, 1962. xxi + 363 pp. Figs. and tables. 16 × 24 cm. $15.

According to the editors' preface, this translation of the second edition of Grinberg's "Vvedenie v Khimiyu Kompleksnykh Soedinenii" is designed to acquaint chemists with Russian work in coordination chemistry and also to serve as an intermediate textbook. It is questionable whether it is really satisfactory for either purpose.

The book was published originally in 1945, and the second Russian edition appeared in 1951; so it contains no information on Soviet research in inorganic chemistry during the last decade. Well over half of the references are to work published prior to 1940. The emphasis on early theories and the descriptive chemistry of coordination compounds together with the lack of any modern discussion of bonding or experimental techniques makes this book virtually a history of coordination chemistry. The second chapter, entitled Coordination Theory, is primarily a discussion of 19th-century ideas and ends with Werner's contributions which were first presented in 1893. Isomerism of six and four coordinate complexes is treated in detail with numerous examples from the compounds of chromium, cobalt, and platinum. The editors have added footnotes to correct some of the most outdated material, and they have also supplied a useful supplementary bibliography to recent works in English.

No discussion of bonding in coordination compounds is given until page 174. There a chapter entitled The Nature of the Force of Complex Formation begins with a discussion of the simple electrostatic calculations of coordination number and the energy of complexes which have been used extensively by Soviet inorganic chemists. Electronic configurations of atoms are then considered for the first time, and a brief discussion of hybridization involving *d* orbitals is given. Students who have not read the article in J. CHEM. EDUC., 29, 2 (1952) may be amused by the comments on the censuring of resonance theory by the chemical society of the USSR.

Experimental evidence for the trans effect is discussed with many examples from the reactions of Pt(II) complexes. Solution equilibria are treated, and the book is concluded with a survey based on the periodic table of the ability of the elements to form complexes. As an example of the approach, hexavalent sulfur, tungsten, and uranium are all treated together in Group VI, so it is rather difficult to provide a coherent discussion of the chemistry of the compounds involved.

It would be difficult to recommend this book for use as a text at any level. Although much interesting descriptive chemistry is presented, this must be separated from all of the obsolete theories, incorrect structures, and improper interpretations of experiments which date from inorganic chemistry prior to the 1940's. For the student interested in descriptive chemistry, Bailar's "The Chemistry of the Coordination Compounds" would seem to be a much better buy even at $18.50 than this book is at $15. On the other hand, the advanced student interested in transition metal compounds may find it interesting to read about the early work in the field and its development in the USSR much as the reviewer did when he originally read the almost identical German translation, "Einfuhrung in die Chemie der Komplexverbindungen," VEB Verlag Technik, Berlin, 1955.

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Progress in Inorganic Chemistry. Volume 3

Edited by *F. Albert Cotton*, Massachusetts Institute of Technology, Cambridge. Interscience Publishers (a division of John Wiley and Sons, Inc.), New York, 1962. 551 pp. 16 × 23.5 cm. $15.

The third volume in this excellent series consists of five articles. As in previous volumes, the subjects range in scope from strictly theoretical presentations to essentially descriptive summaries, although even here the application of theory is not neglected where it may be applied. All subjects are of current interest to the inorganic chemist and will be helpful in keeping him abreast of modern developments in areas in which he may have only a cursory acquaintance. This reviewer feels that collections of this type are becoming increasingly important. Everyone interested in inorganic chemistry should have access to these collected works.

The first article by R. A. Laudice is entitled Hydrothermal Synthesis of Single Crystals. Experimental methods are outlined together with considerations of the advantages and disadvantages of hydrothermal crystallization. Factors of importance in carrying out both crystallizations and synthesis are discussed, including phase equilibria, solubilities, the kinetics of crystallization, and the results of adding impurities. Finally, a compilation of crystals which have been grown by this technique is given, together with outlines of experimental conditions.

A. W. Searcy discusses High Temperature Inorganic Chemistry. This subject seems particularly pertinent, since to the non-specialist the field of high temperature chemistry may seem, as the author points out, "to provide only an uninviting jumble of disconnected data"; yet the importance of the field in modern research and technology can hardly be denied. The author attempts to systematize and generalize the subject and describes some of the patterns of behavior that can be found for systems at high temperatures. In particular the effects of temperature and entropy changes on crystallographic transitions and on reaction equilibria are discussed. The principles are then applied to an analysis of the relative stabilities of binary solids, to the reactions of gaseous hydrides with solids, and to the use of reducing agents whose oxidation products are gaseous. The remainder of the review discusses homogeneous gas reactions and the structure and bonding of these molecules at high temperature.

The third article by D. Seyferth is an exhaustive and critical review of Vinyl Compounds of Metals. The subject is introduced by a discussion of the addition and cleavage reactions of vinyl-metal compounds. This is followed by a discussion of the chemistry of individual metals. Metals considered are: alkali metals, lithium, sodium, and potassium; group IIA, magnesium; group IIB, zinc, cadmium, and mercury; group III, boron, aluminum, gallium, and thallium; group IV, silicon, germanium, tin, and lead; and group V, phosphorus, arsenic, antimony, and lead.

A. D. Liehr presents a theoretical discussion of The Coupling of Vibrational and Electronic Motions in Degenerate Electron States of Inorganic Complexes. Part I. States of Double Degeneracy. The presentation is semi-quantitative and should be readily appreciated by one familiar with the fundamentals of quantum mechanics. Octahedral and tetrahedral complexes are discussed together with the experimental consequences of John-Teller motions which produce distortions in the ideal configurations of inorganic complexes.

In the final article, T. R. P. Gibbs, Jr. discusses the Primary Solid Hydrides. The properties of binary salt-like and metallic hydrides are considered from a theoretical-chemical point of view rather than from purely their chemical and physi-

(*Continued on page A394*)

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APPLICATIONS OF GROUP THEORY IN CHEMISTRY: A Practical Introduction
By F. Albert Cotton, *Massachusetts Institute of Technology*. This book is written expressly for the student of chemistry who wishes to acquaint himself with the basic applications of group theory to chemical problems. It presents a detailed coverage of the essential theory, and explains, with illustrations, its major applications. An Interscience Book. *1963. 295 pages. $12.50.*

TEXTBOOK OF ORGANIC CHEMISTRY
By Alexander Gero, *Hahnemann Medical College*. This book is a *teaching* text, for the average student—one that presents organic chemistry as an exercise in reading and understanding rather than memorization. *1963. 679 pages. $9.50.*

SPECTROMETRIC IDENTIFICATION OF ORGANIC COMPOUNDS
By Robert M. Silverstein *and* G. Clayton Bassler, *both of Stanford Research Institute*. This book shows how to identify organic compounds by recording molecular responses to energy probes as mass, infrared, nuclear magnetic resonance, and ultraviolet spectra. *1963. 303 pages. $8.50.*

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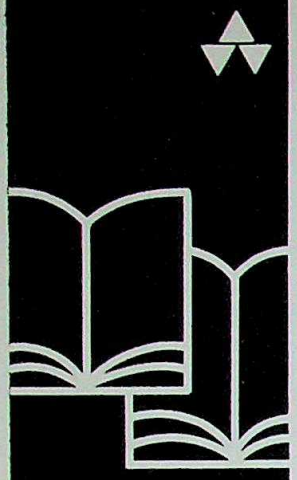
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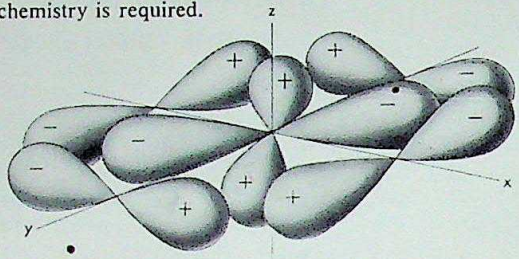
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M. HAÏSSINSKY, Director of Research, C. N. R. S.
Institute of Radium, Paris

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c. 832 pp, 150 illus (1963)

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Oak Ridge National Laboratory

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cal properties. The article is comprehensive and is a small monograph in itself (194 pp.), and should prove an invaluable source of information to those active in the field.

E. CHARLES EVERS
University of Pennsylvania
Philadelphia

Methods in Carbohydrate Chemistry. Volume 1, Analysis and Preparation of Sugars

Edited by *Roy L. Whistler*, Purdue University, Lafayette, Indiana, and *M. L. Wolfrom*, Ohio State University, Columbus. Academic Press, Inc., New York, 1962. xxii + 589 pp. Figs. and tables. 16 × 23.5 cm. $20.

This book is designed to provide the carbohydrate expert with a useful compilation of methods and to provide the non-specialist with an opinion as to the best and most useful methods available. Detailed preparations, reactions and analyses are presented as the best examples from the voluminous fundamental literature.

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(*Continued on page A396*)

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By BERT F. GREEN, Carnegie Institute of Technology. Lincoln Laboratory Publications. Available in June, 1963.

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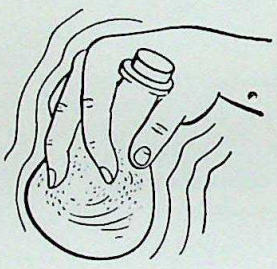
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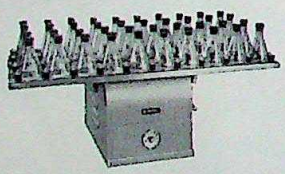


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Fourcroy: Chemist and Revolutionary

W. A. Smeaton, University College, London. Printed for the author by Heffer and Sons, Ltd., Cambridge, 1962. xxi + 288 pp. 14.5 × 22 cm. $6.

The firmament of chemical history is studded with luminaries not of the first magnitude but whose work was an essential factor in the growth of our science. Usually these men are not favored as subjects except by biographers in their own country. Those who are particularly interested in the human side of chemistry are especially grateful when an account such as this appears in English so that all can learn about the life and work of one of these men.

Though A. F. de Fourcroy (1755–1809) was roughly contemporaneous with Lavoisier (1743–94), and though both lived in Paris throughout their lives, Fourcroy's life was uneventful in comparison with the dramatic happenings which marked Lavoisier's career. Fourcroy had to make his living as a poorly-paid lecturer and author of books, which, though widely read, actually brought in but little cash. His position improved when he later was appointed to high government posts, but he was never more than comfortably well off.

Though he was trained in medicine, his career as a practicing physician was brief; however, he was oriented toward the biological sciences by this professional education. Much of his research dealt with animal and vegetable chemistry, and he was a valued civil servant in matters concerned with public health and hygiene. While still a student he showed remarkable ability to lecture on chemistry and allied fields and it was not long before he was giving private courses as a means of livelihood. In time his reputation grew; he was appointed professor at the Jardin du Roi and in due course was recognized as the outstanding lecturer in chemistry in all of France.

Fourcroy was active in the Académie des Sciences from his election in 1785 until 1793 when it was suppressed. Together with Lavoisier, du Morveau, and Berthollet, he developed a new chemical nomenclature which was introduced in 1787 and still serves as the basis of our modern chemical language. He joined with Lavoisier and others in the founding (1789) of the *Annales de Chimie*, which is still appearing and hence is the oldest of our chemical periodicals. He was one of the early converts to the anti-phlogistic theory of combustion and his "Principes de chimie" (1787) was the first textbook of

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Proceedings of a Conference held in Oxford, September 1961

Edited by **R. M. Elliott,** Associated Electrical Industries Limited, Manchester

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chemistry written entirely according to the new theory.

There is no need to give details of Fourcroy's scientific work. There were no startling or important discoveries; he was an indefatigable worker but his forte lay in other fields. The details of his published experiments can be found in the volume here under review. The author has obviously ploughed through the great mass of Fourcroy's published papers, a tedious task which undoubtedly required a goodly supply of patience. He has also discussed at length the principal books authored by Fourcroy and given details of his lecture courses. A chapter is devoted to the work on animal and medical chemistry and a companion chapter deals with the studies on vegetable chemistry. Much of this work as well as that in the inorganic field was done in collaboration with N. L. Vauquelin (1763–1829), the discoverer of chromium. The latter was a better laboratory chemist than Fourcroy (his teacher) and it may well be said that Vauquelin was Fourcroy's greatest discovery.

An outstanding feature of this biography is the Bibliography which contains 342 items written by or about Fourcroy. The author patently has thoroughly combed the literature and the care with which he has done his homework is amply reflected in the excellence of the book. It is proper to point out that he has scrupulously examined the evidence regarding the part played by Fourcroy at the time of Lavoisier's execution and comes to the conclusion that his legal murder was a great shock to Fourcroy, who was helpless to aid his colleague because the latter was one of the detested *Fermiers généraux* and therefore in a hopeless position.

Ralph E. Oesper
University of Cincinnati
Cincinnati, Ohio

Great Chemists

Edited by *Eduard Farber*. Interscience Publishers, Inc., New York, 1961. xxvi + 1642 pp. Figures. 16 × 24 cm. $29.50.

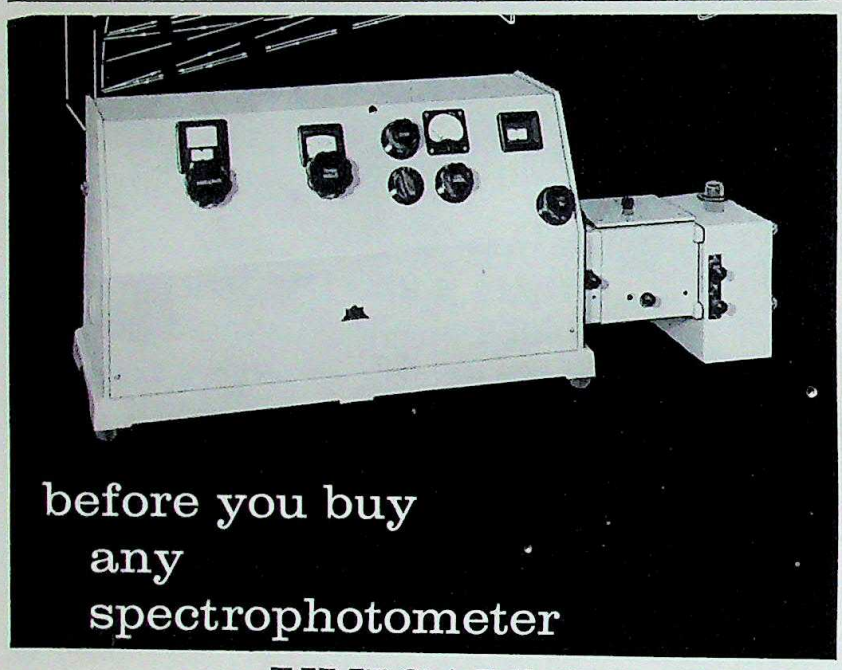
In this imposing and unique volume, Eduard Farber has assembled an impressive collection of biographies by a notable list of contributors. Covering a span of more than three millenia, the entries range from Babylonian Chemists by the specialist in this area, Martin Levey, to E. A. Guggenheim's study of Niels Bjerrum, who died in 1958.

Most of the 114 chapters, 22 of which have been translated by Farber, are devoted to single individuals, but some encompass several chemists, e.g., Aaron Ihde's American Chemists at the Turn of the Century. Almost every chapter is provided with a portrait, unfortunately on annoyingly translucent paper, as is the entire book. Four interludes by the editor, Philosophers and Practitioners, Philosophical Alchemists and Practical Metallurgists, The Chemist's Language, and Scientists and Industrialists add unity to the volume. The chapter titles are sometimes deceptive; the long essay on Armstrong is actually concerned extensively with Laurent, Gerhardt, Frankland, Kolbe, Kekulé, and their theories of chemical bonding. The Table of Contents, therefore, gives only a hint of the scope of the work; one can best tap its gold mine of information by consulting the excellent index from Abbaside to Zosimos.

The essays vary greatly in objectivity, some being obituary notices, eulogies, or memorial addresses, which tend to overevaluate their subject. Often length is not proportional to the importance of the subject. J. R. Partington's scholarly 32-page essay on Joan Baptista van Helmont contains 169 notes and references, while August Kekulé is disposed of in three pages; the Kekulé article is followed, perhaps with poetic justice, by an 11-page essay on Kekulé's unjustly neglected contemporary, Archibald Scott Couper.

European industrial chemists such as Bosch, Perkin, and Solvay are included, but not to the same extent as are Americans, e.g., Baekeland, Dow, Frasch, Little, Midgley, and Teeple, all discussed by the authority on this subject, Williams Haynes. In fact, a legitimate criticism might be the predominance of American chemists, many of whom hardly deserve to rank with such giants as Lavoisier, Berzelius, Liebig, and van't Hoff. One is grateful for the inclu-

(*Continued on page A400*)



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By JOSEPH I. ROUTH, Ph.D., Professor of Biochemistry, State University of Iowa, Iowa City, Iowa. About 480 pages, 6⅝″ × 9¼″, with about 277 illustrations. About $8.50. *New (3rd) Edition—Ready April, 1963.*

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By L. JEAN BOGERT, Ph.D., formerly instructor in the Department of Medicine, University of Chicago; Instructor in Experimental Medicine, Yale University Medical School; and Lecturer in Chemistry, Connecticut Training School for Nurses, New Haven, Connecticut. About 640 pages, 6⅛″ × 9¼″, with about 204 illustrations. About $7.50. *New (9th) Edition—Ready May, 1963*

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sion of studies of less well-known minor figures as Aschan, Ciamician, Duhamel, Klason, and Payen, but one must question how this affects the "balance" of the over-all picture presented. This reviewer wishes that Farber had included separate chapters on Becher and Stahl, Gerhardt and Laurent, Kolbe and Frankland, Guldberg and Waage, and especially Avogadro, without whose law modern chemistry is inconceivable.

Anyone who reads extensively in this book will be impressed anew with the shallowness of the stereotype of the scientist with which the public has been presented. Despite certain recurring resemblances in backgrounds and temperaments, each of the scientists discussed remains known as an individual. Farber has made a commendable effort to present each man of extensive scientific interests such as Ostwald or a specialist such as Claude S. Hudson.

The trend in science has unfortunately been to depersonalize the individual scientist. In our use of the terms Glauber's salt, Dalton's atomic theory, Gmelins Handbuch, Faraday's laws, Bunsen burner, Cannizzaro reaction, Mendeleev's table, van der Waals' equation, Solvay process, LeChatelier's principle, and the Stock system, to mention only an obvious few, we remember the concept but forget the originator; in fact, the proper name has almost been relegated to the status of an adjective. Biographies judiciously introduced into our courses might help to combat the impersonality which many students with artistic and creative tendencies find somewhat repelling about science.

It is a commonplace that many of today's chemists lack a knowledge and appreciation of the history of their science. This reviewer knows of no easier or more pleasant way of remedying this deficiency than by reading Farber's fascinating volume, a worthy English rival to Bugge's German classic, "Das Buch der Grossen Chemiker."

George B. Kauffman
Fresno State College
Fresno, California

Leben und Werk des Chemikers Tobias Lowitz: 1757–1804

N. A. Figurovskij, Academy of Sciences, USSR. Translated into German by *E. Bibow*, Institut für Geschichte an der Deutschen Akademie der Wissenschaften, East Berlin. Akademie Verlag, Berlin, 1959. xi + 159 pp. 16 × 24 cm. 19.50 DM.

The name Tobias Lowitz has practically disappeared from the chemical literature and even the histories give little if any attention to the life and work of this interesting and productive German-Russo apothecary-chemist. In fact, there have been only two previous presentations of his career (A. N. Scherer (1820) and Paul Walden (1901)). Neither of these was adequate and it is therefore a pleasure to welcome the volume under review, which is based on a thorough reading and digestion of all that has been written by and about Lowitz.

His lifespan was only 47 years, he did not begin to publish until he was almost 30, so that the 179 papers (listed in the complete bibliography) appeared during approximately 17 years. They dealt with all branches of chemistry. Some of the procedures he developed for the preparation of pharmaceutical items are still in use, though he is seldom given credit for these advances. He combined chemical theory (so far as it existed) and practical application when he could. He made constant efforts to find ways of increasing the consumption of Russian raw materials and of substituting domestic for foreign products. For example, he sought to obtain sucrose from honey, and as a result found that it owed its sweetness to another substance (invert sugar) and he often served his fellow academicians tea sweetened with his newly-discovered product.

Only a selected few of his numerous discoveries and accomplishments can be noted here. His work on crystallization is outstanding. His wax models of numerous crystals are still on exhibition. He discovered isomorphism, a phenomenon later rediscovered by Mitscherlich to whom the credit is usually given. He was the first to prepare anhydrous ethyl alcohol and also ethyl ether. There are strong indications that he independently discovered strontium and chromium. He distinguished between crystallizable and gluey or soaplike materials, thus anticipating Graham's colloids and crystalloids. These "firsts" demonstrate his standing as a gifted and industrious chemist.

The reviewer is fully aware that this biography was written by a Soviet his-

(*Continued on page A402*)

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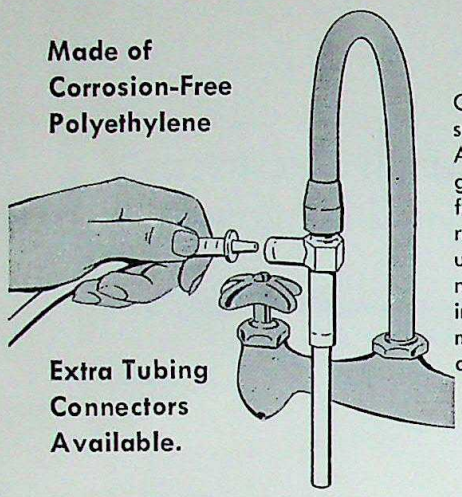
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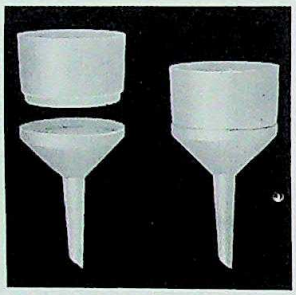
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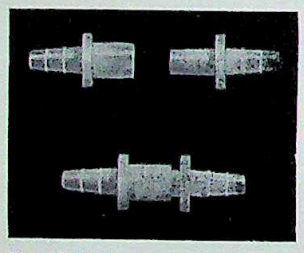
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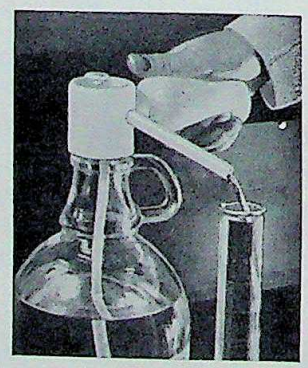
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BOOK REVIEWS

torian about the accomplishments of an early Russian scientist. Perhaps objections may be made to many of the priority claims it contains. It is the duty of a reviewer to tell what the book contains, not to vouch for the accuracy of those contents. The reviewer regrets that an English translation is not available; if it were it should be required reading for young chemists and students, as well as their elders, because it presents a fine account of how a man of insight and interest, along with assiduity, can turn out important work with a minimum of supplies and equipment.

RALPH E. OESPER
University of Cincinnati
Cincinnati, Ohio

Organic Chemistry Laboratory Operations

W. B. Renfrow and *P. J. Hawkins*, both of Oberlin College, Oberlin, Ohio. The Macmillan Co., Inc., New York, 1962. viii + 216 pp. Figs. and tables. 21.5 × 27.5 cm. $3.75.

We are ready for a new kind of laboratory manual in organic chemistry. Such a book will include a basic change in the approach to laboratory instruction as well as presenting the fundamentals of the newer organic techniques.

Renfrow and Hawkins have made a start in this direction primarily by adding some newer techniques to the conventional laboratory course. They also have just a glimmer of an improvement in approach in their device of giving only minimal directions for four elementary experiments; the student is expected to apply the techniques he has acquired in these four preparations.

The book is unified in that theory and practical procedures are combined in each experiment. Theoretical treatments are not as exhaustive as, say, Robertson and Jacobs, but seem to be as extensive and as well written as other soft cover laboratory manuals.

The first two-thirds of "Laboratory Operations" is conventional in its organization and much of its content. Beginning with very uninspired technique experiments (which are no worse than most other manuals), the book moves to preparative work with butyl bromide (still being refluxed for one hour, even 13 years after Joseph's publication in THIS JOURNAL!), and finishes page 130 after qualitative organic analysis. There are a few novel experiments, such as the sequence from cyclohexanol to *N*-(benzenesulfo)-6-aminocaproic acid [sic] which involves a Beckmann rearrangement.

Renfrow and Hawkins contribute a breath of fresh air to the laboratory in the latter third of their text when, in addition to the new conventional treatment of several types of chromatography and advanced distillation, they present hydrogenation (unfortunately the Brown technique had not been discovered when the book

(*Continued on page A404*)

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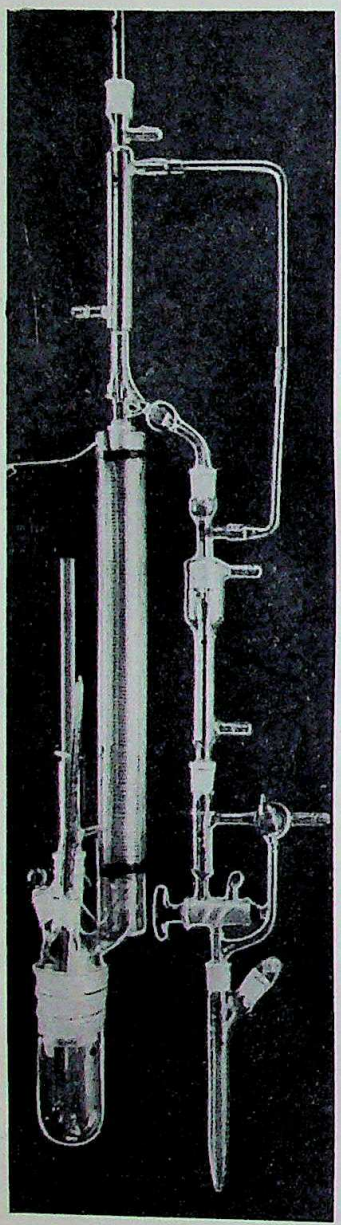
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BOOK REVIEWS

was written), the use of punched cards for filing and recovering information, determination of physical properties (such as density, refractive index, optical rotation, and especially absorption spectroscopy), and finally an experiment on the determination of dissociation constants and one on rate constants (the decomposition of an *N*-bromoamide in base).

The theoretical and practical introduction to spectroscopy is brief but it is very well done in this space and at this level. It is made extremely usable for all schools by the inclusion of seven pages of large spectra accompanied by six unknown spectra for the student to identify. In this Renfrow and Hawkins will be copied by every future manual writer, and the next edition of the Renfrow-Hawkins book will contain NMR. A simplified schematic of IR and UV spectrophotometer would have been useful, although there is a sketch of the basic elements of all such devices.

In any text it is very easy to find details to criticize. A six and one-half line experiment on the use of a spinning band column (without any line drawing and with a reference which does not mention spinning band columns) should either be expanded or deleted. With the number of half-blank pages in the text, there could easily have been twelve more pages of content at little added cost. But I believe that there are only two major flaws in this manual: the almost complete lack of problems and questions during and after each experiment (usually one lone problem follows each) and the type of pedagogy exemplified by the experiment involving filling in blanks for the solubilities of six compounds in six solvents. I am sure that the authors make up for these flaws in their own laboratory instruction, but they should have done it for the rest of us. Their book is too good to condemn just on this account.

The pleasantly gay cover enfolds a good job of bookmaking. The binding is much sturdier than it looks and the typography is decidedly superior to most laboratory manuals. The pages can be torn out and are punched with three holes although the authors (wisely) do not recommend a loose-leaf notebook system.

Frank L. Lambert
Occidental College
Los Angeles, California

High Polymers. Volume 15, Radiation Chemistry of Polymeric Systems

Edited by *Adolphe Chapiro*, Laboratoire Aristide-Briand, Bellevue, France. Interscience Publishers (a division of John Wiley and Sons, Inc.), New York, 1962. xvi + 712 pp. Figs. and tables. 16 × 23.5 cm. $21.

Whenever the subject matter of a scientific treatise combines two different and highly specialized branches of science such as radiation chemistry and polymer

(*Continued on page A406*)

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— while realising that the number of journals in the field of chemistry is considerable,

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chemistry, the author is put to a difficult choice. Since he cannot possibly, without sacrificing consistency, introduce the subject to specialists in both fields, he must decide from the beginning which group he will address primarily. Since this book was to be published as Volume 15 of a "Series of Monographs on the Chemistry, Physics, and Technology of High Polymeric Substances," it was decided—fortunately from the chemist's point of view—to write the book as an integral part of modern polymer chemistry. This required that a substantial part of the book had to be devoted to radiation chemistry, especially the various forms of interaction between matter and the different types of radiation. On this broad basis, which will be welcomed by all chemists who are not too familiar with the recent developments in radiation theory and techniques, the author builds from the large amount of published experimental data a well-ordered and rigorous scientific system that interprets the known facts and figures more consistently than numerous theories created *ad hoc* by many investigators.

The natural starting point for the essential part of the book is the radiation chemistry of hydrocarbons in which the olefinic compounds are discussed in great detail. The spectacular advances that very recently have been made in the radiation of acetylenic compounds are not yet reflected in the text. After exhaustive discussion of radiation-induced polymerization of liquid monomers in homogeneous and heterogeneous phase, the author deals with radiation effects on solid polymers and the irradiation of polymer solutions. The author has freed himself from the tendency to reduce all radiation-polymerization phenomena to free radical reactions, and assigns molecular and ionic mechanisms a proper place. The last chapter of the book is devoted to graft polymerization which recently has found increasing practical applications in many fields. Here would have been the place to mention a most promising new field, namely the direct conversion of wood and wood waste soaked in monomer solution by powerful gamma-rays into a host of useful products.

No other book on radiation polymerization can compare in comprehensiveness, theoretical precision, and practical usefulness with this treatise. Many chemists—not only those specializing in polymer or radiation chemistry—will want to have it for study and permanent reference.

Francis Joseph Weiss
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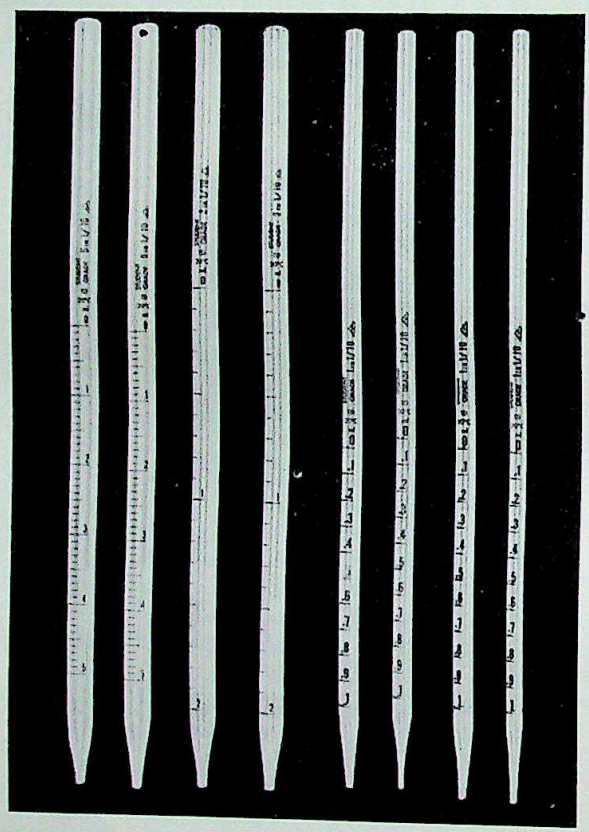
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Experimental Physical Chemistry

Farrington Daniels, J. W. Williams, Paul Bender, Robert A. Alberty, and *C. D. Cornwell,* all of the University of Wisconsin, Madison. 6th ed. McGraw-Hill Book Co., Inc., New York, 1962. xv + 625 pp. Figs. and tables. 16.5 × 24 cm. $7.95.

This edition presents essentially the same experiments as in Part I of the Fifth Edition. A few experiments have been pruned, and there has been some regrouping of material, e.g., the chapters on conductance of electrolytic solutions and electrode phenomena have been combined into one unit entitled Irreversible Processes in Solution and assorted experiments have been gathered under new headings such as Surface Chemistry. Important additions are sections offering experiments in powder X-ray diffraction and molecular spectroscopy which cover more than fifty pages of material. These topics introduce the student to methods which are central to much of modern physical chemistry. The view is taken that the student should cope with data obtained from various less common and more expensive spectrometers even though he may not personally manipulate the "black boxes" which are used to obtain this data. Other new experiments include spectrophotometric determination of equilibrium constants, Knudsen cell vapor pressure determination, kinetics of bromination of acetone, activity coefficients from freezing-point depression data, determination of the dielectric constant of a solid as a function of temperature, and optical rotatory dispersion measurements at three wavelengths.

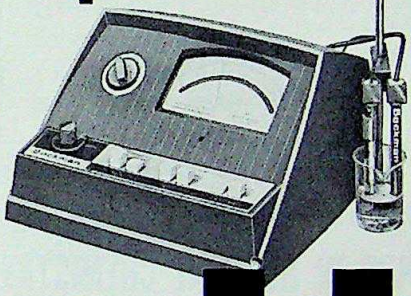
Part II, Apparatus and Methods, includes the material of the preceding editions with some minor changes and two important additions. A new 23-page

(*Continued on page A407*)

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section on spectroscopic methods discusses concepts such as resolution, bandwidth and response time, and the principles of operation of radiofrequency and optical spectrometers. The second major improvement is that the section on electronics in the fifth edition has been more than doubled in this revision. Ac circuit theory is treated using complex algebra, and there are discussions of semiconductor devices, noise phenomena, and a useful coverage of assorted electronic circuits for power supplies, phase sensitive detectors, pulse circuits, and electronic measurements.

It is the feeling of this reviewer that the new sections on electronics, necessary for most physical chemical research work, and molecular structure and spectra help to meet serious deficiencies in the previous edition and introduce the student to work which has occupied a large core and physical chemistry in the last twenty years.

JOHN P. CHESICK
Haverford College
Haverford, Pennsylvania

Solvolytic Displacement Reactions

Andrew Streitwieser, Jr., University of California, Berkeley. McGraw-Hill Book Co., Inc., 1962. ix + 214 pp. Figs. and tables. 16 × 23.5 cm. $5.

As indicated in the introduction the major portion of this book is a verbatim reprint of the author's 1956 *Chemical Reviews* article. The new portion of the book occupies only 22 of 185 text pages. This article contains extensive reviews of the literature of S_N1 and S_N2 reactions and internal displacements, as well as briefer discussions of a number of related reactions. The effect of solvent, nucleophile, and substrate structures are all discussed. The author not only reviews the literature in this outsized field but also provides new insight into many aspects of it. Examples are his illuminating treatment of the effect of conjugation and his provocative, unitarian, view of S_N1 and S_N2 reactions.

The new portion of the book contains brief but up-to-date discussions of Winstein's work on special salt effects, α-hydrogen isotope effects, and non-classical carbonium ions. It has a particularly effective discussion of Hammond's postulate, pointing out that it applies to *nuclear* coordinates, not *electronic* coordinates.

The only omission which strikes the reviewer is a discussion of displacement reactions at atoms other than carbon.

There is no doubt that this book belongs in the library of every chemist who does *not* have access to the original review article. Most, however, will find that article readily available in their libraries, and they will have to decide for themselves whether they care to pay five dollars for a reprint plus 22 pages of new material.

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ZONE REFINING

A Chem Ed TESTED DEMONSTRATION

Rewritten from: John D. Christian, J. CHEM. EDUC. **33,** 32 (1956), by Robert Greve, Far Eastern Highland Mission Island Academy, Agana, Guam

PREPARATION

Prepare a sample for refining by dissolving a trace of methyl red indicator in 6–8 g of molten naphthalene (if only indicator solution is available, a few drops may be carefully evaporated and then the naphthalene melted in the same evaporating dish). The resulting liquid should be a light red-orange in color. Prepare an elongated ingot of the sample drawing the melt into a 15–20 cm length of 6-mm Pyrex tubing and allow it to solidify and sealing one end. The sample should not be drawn closer than 3–5 cm from the end of the tube to be sealed.

Wrap one layer of asbestos paper around a piece of 8-mm Pyrex tubing 8–10 cm long. Wrap $^1/_2$ of a 4.75 ft length of No. 30 nichrome wire tightly around the asbestos to form a coil 1 in. in length near the center of the asbestos covered tube. Cover the coil with a second layer of asbestos and wind the balance of the wire over the first coil. Cover the finished coil with another layer of asbestos.

Clamp the coil in a vertical position, arrange a clock mechanism (electric or spring powered) above the mounted coil, provide a 1-in. circumference bushing over the hour hand shaft (a piece of wooden dowell or a piece of heavy walled rubber tubing). Connect the tube containing the ingot by means of a string to the shaft of the hour hand and adjust so that the ingot will be pulled through the heating coil at a rate of 1 in. per hr. Provide a 10 v power supply (a variable transformer is useful).

DEMONSTRATION

Connect the furnace to its source of power and start the clock. As the ingot is raised through the heating element, a molten zone is formed, and recrystallization occurs at the upper end as the material cools. The recrystallized material will be colorless, and the color impurities will collect in the molten zone.

REMARKS

The process is readily adaptable to the purification of a variety of substances, and the required temperature can be readily attained by adjusting the voltage applied to the coil.

PARAMAGNETISM

A Chem Ed TESTED DEMONSTRATION

Submitted by: Yu-tsai Peng, Chinese Military Academy, Fengshan, Republic of China

Checked by: Robert Greve, Far Eastern Highland Mission Island Academy, Agana, Guam

PREPARATION

Provide an Alnico magnet (Cenco 78236-C or equivalent), a glass dish, distilled water, dropper, and a freshly prepared mixture made by mixing equal volumes of 0.5 *M* $FeCl_3$ and 0.5 *M* $K_4Fe(CN)_6$. Also provide two droppers calibrated to deliver 0.04 ml per drop and a piece of glass tubing 8 × 200 mm with a right angle bend approximately 2 cm from each end.

DEMONSTRATION

Place the magnet in the glass dish, add a thin layer of water, and allow to stand at rest for approximately 10 mins. Add one drop of the freshly prepared blue mixture approximately 1 cm from the poles of the magnet. The blue complex will diffuse into the magnetic field.

Mount the glass tube in a horizontal position so that it is level. Fill the tube with distilled water until it just enters the bent portion at each end. Carefully add one drop of $FeCl_3$ and one drop of $K_4Fe(CN)_6$ to opposite ends. Observe the position of the blue ring formed as the result of the diffusion. As soon as the blue band forms, position the Alnico magnet adjacent to the tube and to the right of the band. The band will slowly move into the magnetic field.

REMARKS

The position of formation of the blue ring can be displaced by placing a strong magnet at one end of the glass tube.

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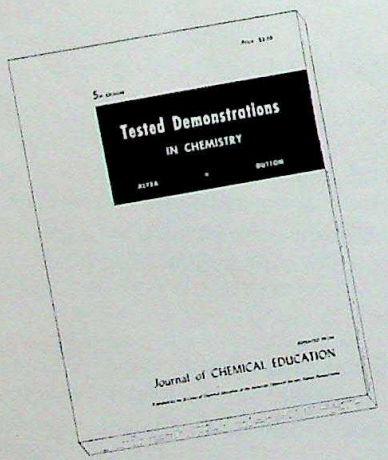
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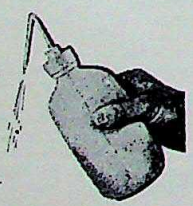
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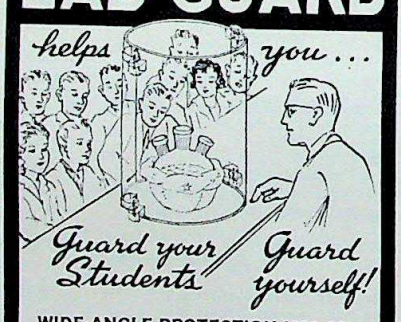
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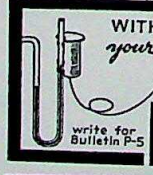
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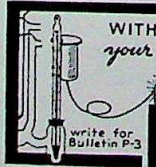
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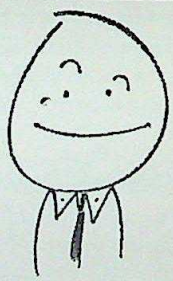
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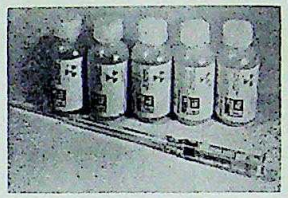
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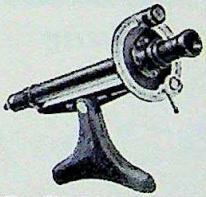
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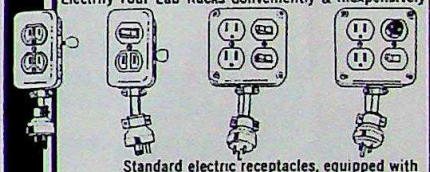
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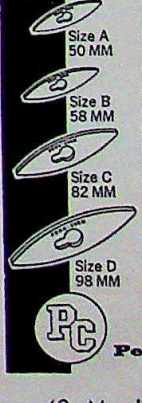
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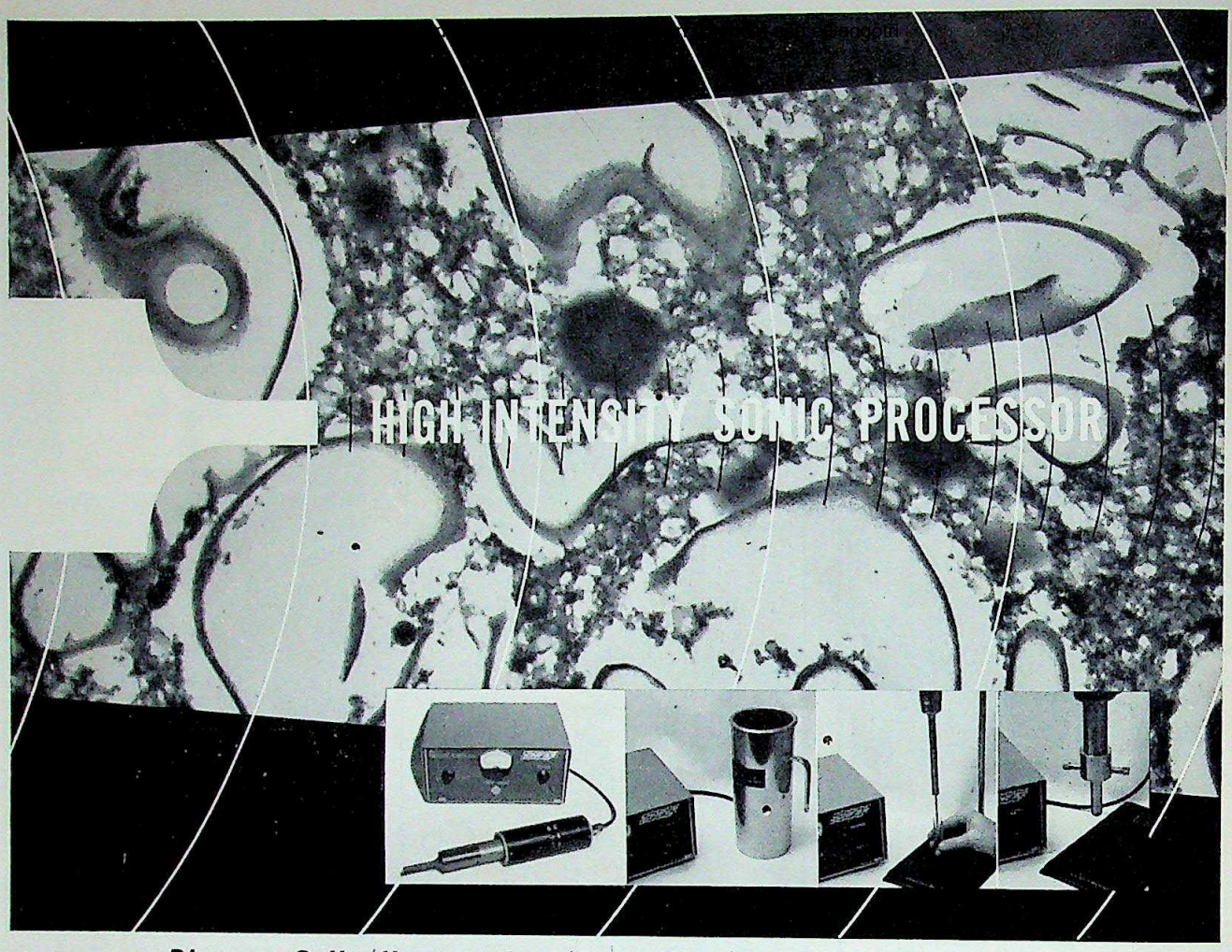
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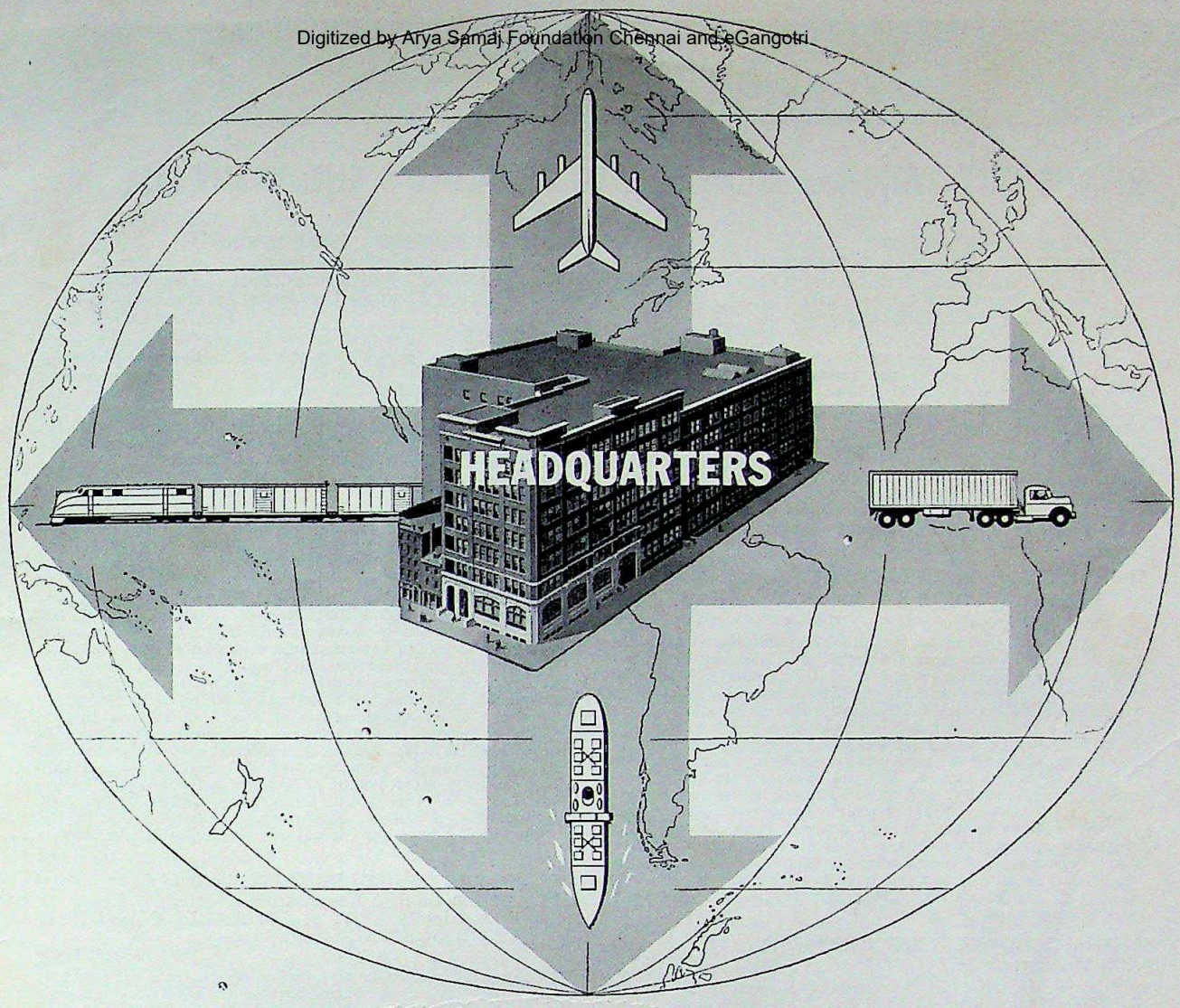
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These articles, most of which are to be contributed by guest authors, are intended to serve the readers of this JOURNAL *by calling attention to new developments in the theory, design, or availability of chemical laboratory instrumentation, or by presenting useful insights and explanations of topics that are of practical importance to those who use, or teach the use of, modern instrumentation and instrumental techniques.*

VIII. Instrumentation for Particle Size Analysis. Part Three.

S. Z. Lewin, *Department of Chemistry, New York University*

The preceding sections have treated the principles of design and application of instrumentation for the determination of the sizes of the particles in a specimen by means of (*a*) the dispersal and measurement of the individual particles, and (*b*) the distribution of the sample into fractions composed of particles falling into more or less well-defined size ranges. A third category of instrumental techniques is available, in the application of which the sample is neither dispersed nor fractionated, but rather a physical or chemical measurement is made that yields information related to some kind of average either of the area or volume of the particles, or of that of the voids or inhomogeneities in the sample. Hence, this type of approach may be characterized as based upon the measurement of an *integral property* of the sample. Although this kind of measurement is only capable of yielding information about some averaged (i.e., integrated) size-dependent parameter, it is possible, in some cases, to make the measurement under several different conditions, such that the relative contributions to the over-all average made by different sized particles changes with the conditions of the experiment. Such data can then often be interpreted to yield some insights into the distribution of particle sizes in the sample.

Integral Property Techniques

A considerable number of properties is sufficiently sensitive to the dimensions of particles or of the voids between (or within) them to be potentially useful for particle size analysis. The following list summarizes the properties that have been accorded serious attention in this respect.

1. *Line Broadening of X-Ray Diffraction Pattern.* If the particle size of the crystallites bathed in an x-ray beam is of the order of 0.1 micron and less, the Bragg reflections (i.e., the intensity maxima governed by the Bragg law, $n\lambda = 2d \sin \theta$, where θ is the angle made by the incident beam, of wavelength λ, with the set of planes whose interplanar separation is d) broaden out. This is due to the fact that when the number of crystal planes contributing to a diffraction peak is not large, the peak loses its sharpness, just as the resolving power (i.e., sharpness of spectral lines) of a ruled diffraction grating diminishes as the area illuminated is decreased. It has been shown for a monodisperse sample (i.e., one in which all the particles are of the same size) that the line broadening, defined as the width of the line at half its maximum intensity, is related to the thickness of the crystallites by the formula:

$$t = \frac{0.9\,\lambda}{B \cos\theta}$$

2. *Small Angle Scattering of X-Rays.* If the intensity of x-radiation scattered by a sample is measured as a function of angle close to the direction of the undeviated beam, it is observed that the manner in which the intensity falls off with increasing angle is sensitive to the dimensions of the inhomogeneities present in the sample. This effect is illustrated by the curves shown in Figure 20, which are calculated on the basis of scattering theory. At a given scattering angle, some x-rays reach the detector from particles, and others from voids in the sample. The degree of mutual interference suffered by the various rays coming to a given point at each scattering angle depends upon the relative sizes and numbers of these two types of scattering centers.

3. *Scattering of Visible Light.* The intensity of the light scattered by particles suspended in a medium of different refractive index is a function of the angle of viewing, wavelength of the light, and shape and size of the particles. The complex nature

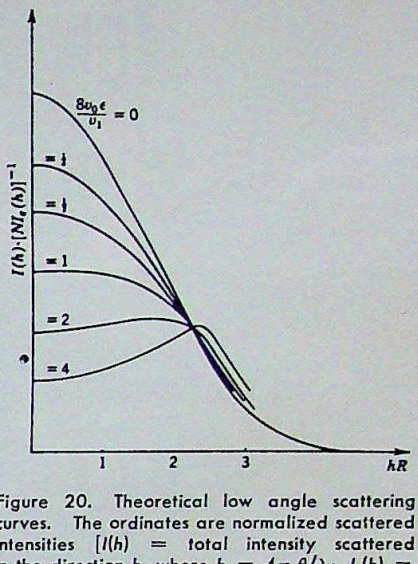


Figure 20. Theoretical low angle scattering curves. The ordinates are normalized scattered intensities [$I(h)$ = total intensity scattered in the direction h, where $h = 4\pi\,\theta/\lambda$; $I_e(h)$ = intensity scattered in the direction h by a single electron; $\bar{N}$ = number of particles]. The abscissae are proportional to the scattering angle [$hR = 4R\,\pi\,\theta/\lambda$, where R is the particle radius]. Each curve refers to a different ratio of the particle size to the size of the interparticle spaces [v_0 = volume of particle, v_1 average volume of sample available to each particle, i.e., V_0/N, where V_0 is the total volume of the sample; ϵ is a constant that is approximately unity]. From Guinier, A., and Fournet, G., "Small-Angle Scattering of X-Rays," John Wiley and Sons, N. Y., 1955.

of the interrelationships among these factors is illustrated by the diagram of Figure 21, which shows the variation of intensity with angle for monochromatic light scat-

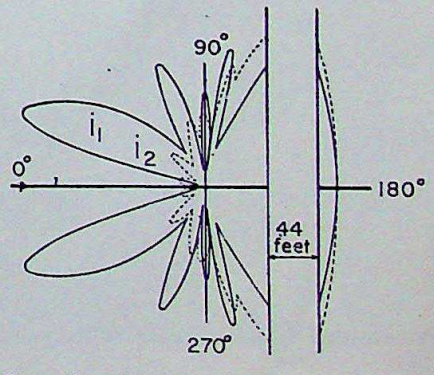


Figure 21. Variation of scattered intensity of light of wavelength λ about a spherical particle of radius r when $2\pi r = 8\lambda$, and refractive index of the particle is 1.25. The full line, i_1, gives the intensity of the vertically polarized component of the scattered light; the dashed line, i_2, refers to the horizontally polarized component. From Blumer, H., *Z. Physik*, 32, 124 (1925).

tered by a particle larger than the wavelength of the light. If the particle size is

(*Continued on page A425*)

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smaller than the wavelength of the light, the scattering pattern is much more uniform, although the intensity in the forward direction remains greater than that in the backward or sideward directions. For such particles, the scattering pattern tends to become independent of the shape of the particles.

If the particles are smaller than 0.02 microns in radius, and are in a dilute suspension in a medium of refractive index n, the turbidity, T, is expressed by the Debye equation:

$$T = -\log \frac{I}{I_0} = \frac{32\pi^3}{3\lambda^4}\left(\frac{dn}{dc}\right)^2 \frac{n^2 Mc}{N}$$

where I is the transmitted intensity, I_0 the incident intensity, M the molecular weight, c the concentration in g/cm³, λ the wavelength of the light in air, N the Avogadro number, and dn/dc is the refractive index increment of the medium due to unit increase in concentration of the suspended phase.

The particle sizes of monodisperse samples can be determined through measurements of turbidity, scattered intensity at selected angles, angular variation in the color of the scattered radiation when white incident light is employed, or relative intensities of the vertically and horizontally polarized components in the scattered radiation. For polydisperse samples only the turbidity is commonly employed, and it is related empirically to particle concentration and average size.

4. *Pressure Drop Under Streamline Flow.* If a fluid (gas or liquid) is caused to flow through a porous sample, such as a compacted powder, the pressure drop, $P_i - P_0$, across the plug of length L is given by the expression:

$$\frac{P_i - P_0}{L} = \frac{2\eta v S^2}{g}\frac{(1-\alpha)^2}{\alpha^2}$$

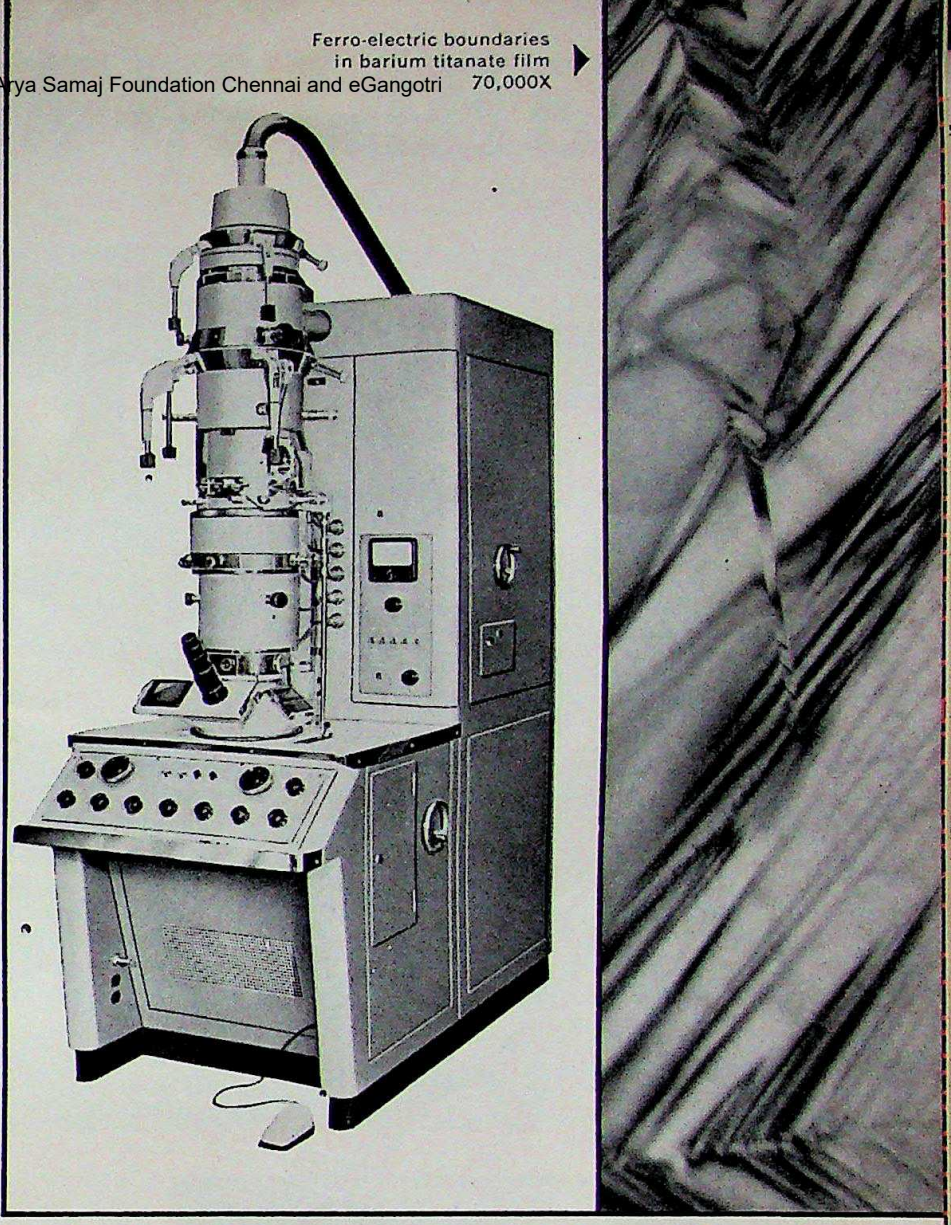
where η is the viscosity of the fluid, v is the velocity of flow, S is the surface area per unit volume of the powder or porous solid, g is the gravitational constant, and α is the fraction of voids, i.e., $\alpha = V_v/V_t$ where V_v is the volume of voids in the plug and V_t is its total volume.

5. *Knudsen Flow Rate.* When the size of the voids in a plug is small in comparison with the mean free path of the molecules of a gas flowing through the plug, the rate of flow is limited only by collisions of gas molecules with the solid surfaces, and not by collisions occurring between gas molecules. This is the condition of molecular streaming, or Knudsen flow, and the flow rate is considerably greater than for streamline flow. Measurements of the flow rate under these conditions can therefore be related to the mean dimensions of the pores and voids in the sample.

6. *Gas Adsorption.* If the adsorption of a gas on a solid surface is due principally to van der Waals forces, as, e.g., in the adsorption of nitrogen on various solids at liquid nitrogen temperatures, the volume adsorbed as a function of the pressure, p, can be expressed by the Brunauer, Emmett, and Teller (BET) equation:

(*Continued on page A428*)

Ferro-electric boundaries in barium titanate film 70,000X



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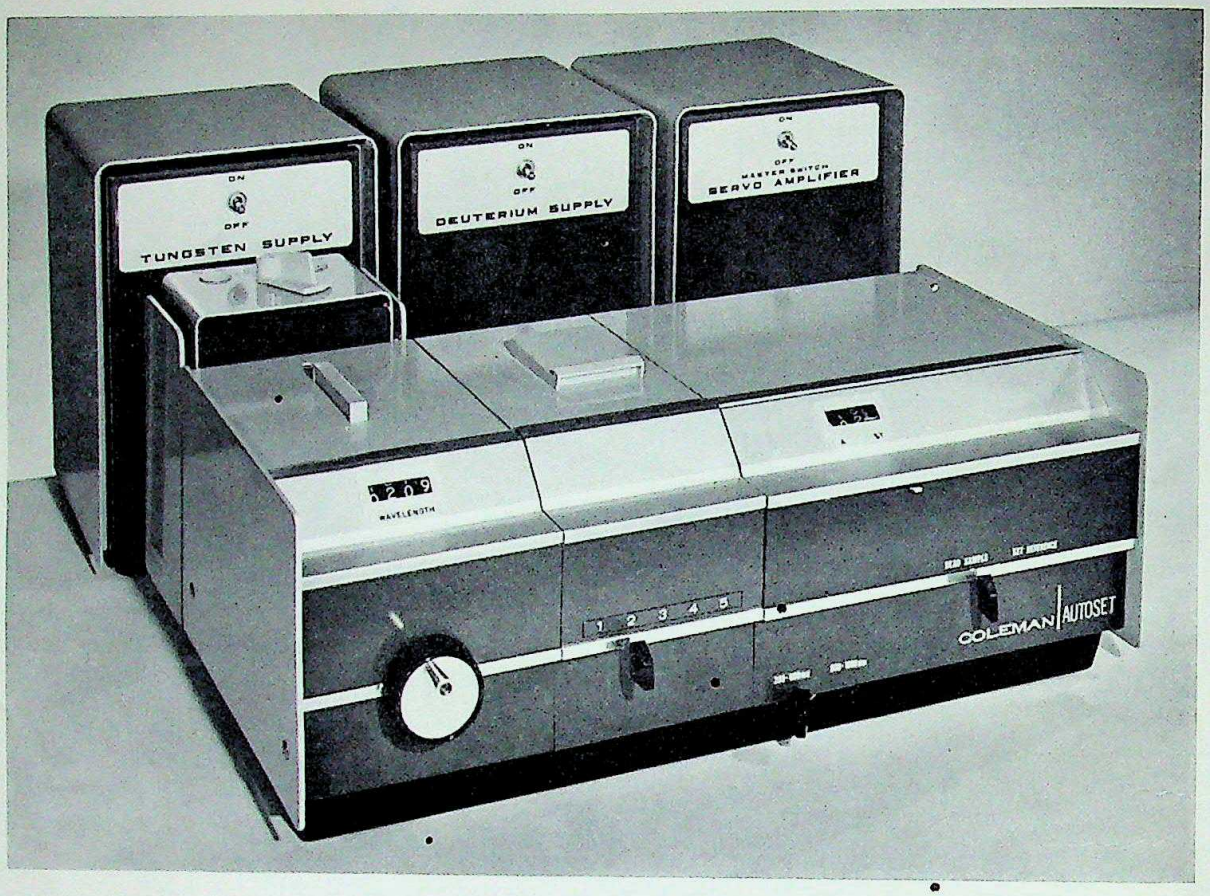
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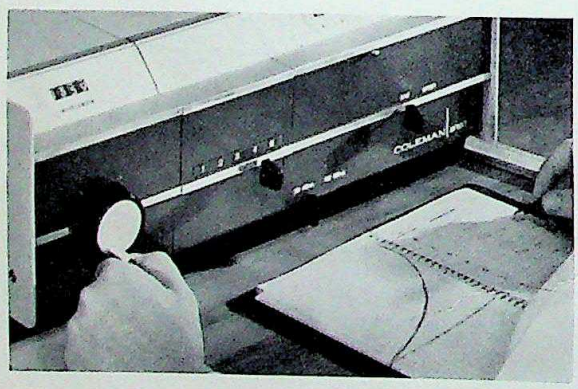
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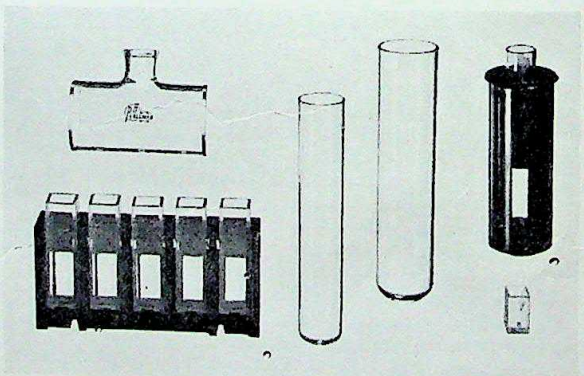
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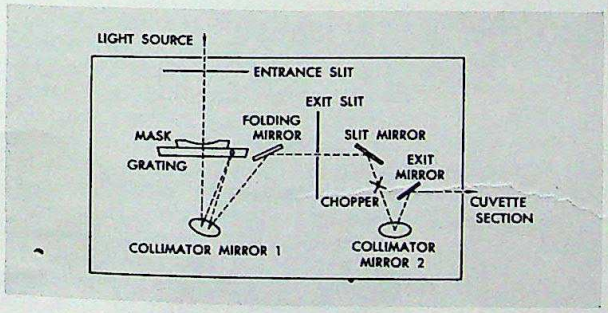
★ ***bipartite diffraction grating optics***

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2 millimicron standard bandwidth; 1 and 5 millimicron bandwidths also available for special work.
Wavelength range 200-1000 millimicrons.

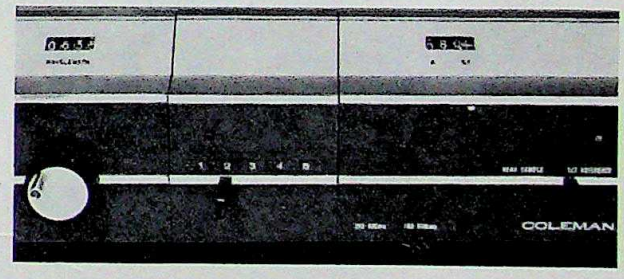
Photometer
Self-balancing null system.
Photometric accuracy: ±0.05%T, ±0.005A at 0.4A.

Sample range
120 microliters to 25 milliliters.
1 to 100 millimeter light path.



Bipartite diffraction grating optics

The Coleman AUTOSET Spectrophotometer provides the laboratory with the practical advantage of a working instrument with the analytical range of a specialized research equipment. A bipartite diffraction grating, dual light source, and dual phototubes provide high levels of energy throughout the 200-1000mμ spectrum. The bipartite grating produces a straight and linear spectrum which provides constant band width at all wavelengths, with fixed optical slits. Constant band width insures maximum reproducibility.



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$$\frac{p}{V(p_s - p)} = \frac{1}{V_m C} + \left(\frac{C-1}{V_m C}\right)\frac{p}{p_s}$$

where p_s is the saturation pressure of the gas, V_m is the volume of gas adsorbed when a monomolecular layer has been formed, and C is a constant. Figure 22

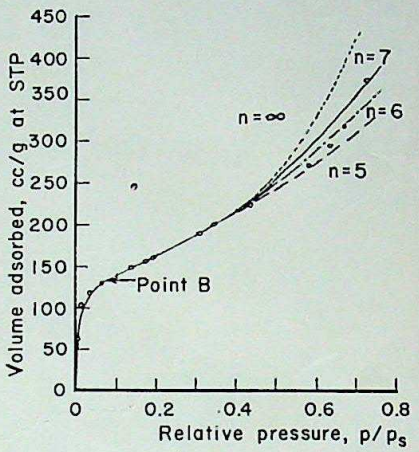


Figure 22. Adsorption isotherms as calculated from BET theory for cases in which the existence of pores or capillaries limits the maximum number of molecular layers of adsorbate to the values shown. Point B corresponds to the completion of a monolayer. The circles show experimental points obtained for the adsorption of nitrogen on a sample of iron powder. From Brunauer, S., "The Adsorption of Gases and Vapors," Princeton University Press, 1943.

shows the forms of the calculated adsorption isotherms for several cases in which the maximum number of layers of the adsorbed gas varies from 5 to ∞ (the BET equation in the form given above applies specifically only to the latter case). Point B in the figure corresponds to the relative pressure at which a completed monomolecular layer has been formed. The volume of gas corresponding to a completed monolayer is obtained from the plot of $p/V(p_s - p)$ versus p/p_s, and is in turn employed to calculate the total surface area of the sample.

When the adsorption is not adequately described by the BET equation, other semi-empirical approaches may be adopted for relating the variation in volume of gas adsorbed as a function of the relative pressure to the surface area of the adsorbing solid.

The rate of adsorption, e.g., $-dp/dt$ in a constant volume system, may be measured in place of the total amount of adsorption.

7. *Adsorption of a Solute from the Liquid Phase.* The adsorption of certain solutes on the surfaces of certain solids shows a definite saturation value, as shown in Figure 23, and this suggests that under these conditions a monolayer of adsorbed molecules has been formed. Determination of the decrease in concentration of the solution at the plateau can, on the basis of this assumption, be utilized to compute the total surface area of the solid phase.

(*Continued on page A430*)

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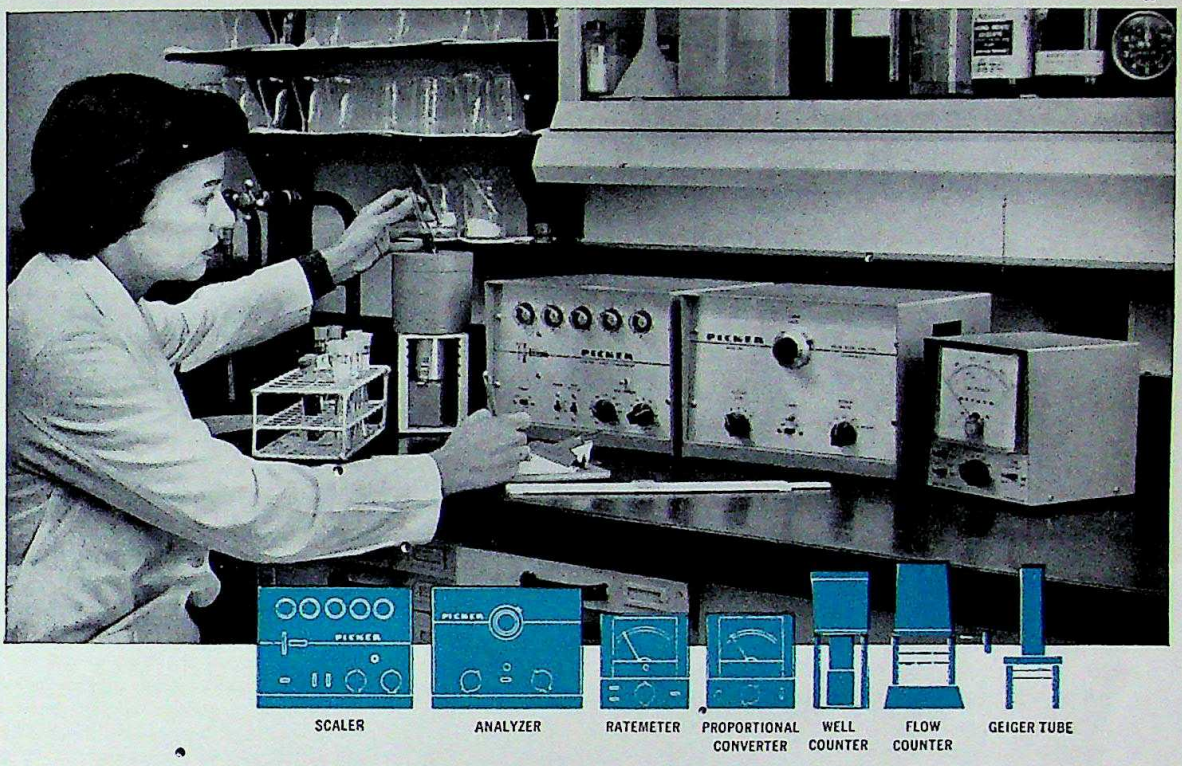
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NEW DIMENSIONS IN GAS TECHNOLOGY

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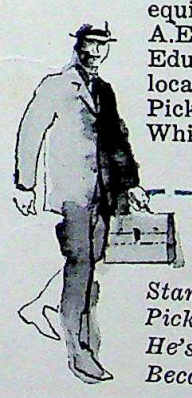


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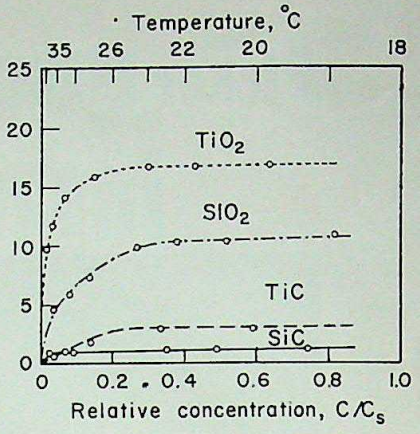


Figure 23. Adsorption isotherms of stearic acid in benzene solution on several solid powders. The ordinates are milligrams of solute adsorbed per gram of solid phase. The abscissae at the bottom are relative concentration, i.e., the ratio of the concentration of the solute to its saturation concentration. The abscissae at the top show the corresponding quantities in terms of the temperature of a solution of fixed composition.

Equivalent results have been obtained in some cases with the adsorption of dyes from solution, and this technique has been widely used because of the ease with which the concentration changes that occur can be determined by colorimetry or spectrophotometry.

8. *Radioactive Tracer Exchange.* It has been suggested that if radioactively labeled species in solution can be exchanged for non-radioactive species in the surface of a solid phase, the decrease in radioactivity of the solution, or the pick-up of activity of the solid, can be utilized to yield the total surface area. However, this method is limited to cases in which it can be established that the exchange does not penetrate below the surface layer, and that recrystallization or local cell effects are absent.

9. *Absolute Calorimetry.* If a solid is allowed to become coated with a layer of an adsorbed liquid which is in equilibrium with the saturated vapor of that liquid, then upon immersing the solid into a reservoir of that same liquid, an amount of heat would be liberated that is equal to the total surface energy (i.e., surface tension × total area) of the adsorbed liquid, since the surface of the latter disappears during this process. Since the surface tension of the adsorbed liquid can be presumed to be known, calorimetric determination of the heat of immersion can be employed to yield values of the surface area of the solid. This approach is often designated as the Harkins-Jura absolute (HJa) technique. The method is considered to be absolute since it does not depend upon an assumption as to the area occupied on the surface of the solid by each molecule of adsorbate.

10. *Other Techniques.* Other parameters that have been shown to be related to surface area or particle sizes are: relationship between magnitude of applied suction and amount of water removed

(*Continued on page A432*)



ONLY THIS B&L SPECTRONIC 20 COLORIMETER combines the fastest, most accurate colorimeter you can buy—with complete spectrophotometric capability for transmission and reflectance studies throughout the 340mμ-950mμ range—*for less than the price of most colorimeters alone.* Just dial the wavelength you need. That's all there is to it. No filters, no fussing with slit width or sensitivity controls. The Certified-Precision Grating, with constant 20mμ bandpass, instantly delivers monochromatic light of spectral purity unattainable with any other instrument . . . at even four times its low price. See for yourself, in your own lab.

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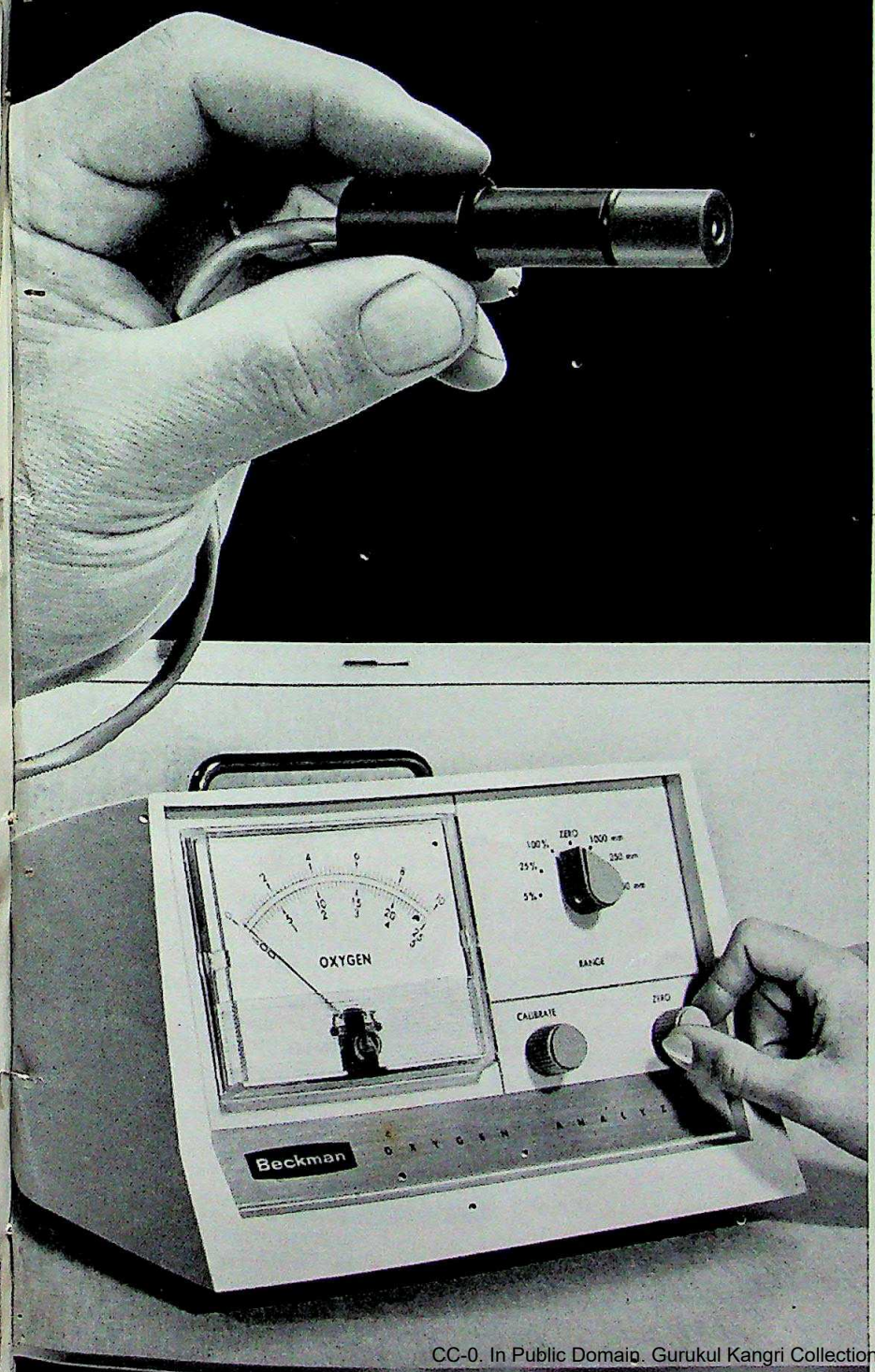
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from a water-saturated packing of the specimen; conductivity of heat through a packing of the specimen; variation of the amount of heat evolved due to adsorption of a gas as a function of the time it is left in contact with the sample; rate of dissolution of the solid under conditions such that the rate of dissolution is limited by the diffusion of saturated solution away from the surface of the solid; rate of emanation of a volatile daughter element from a solid containing a radio-

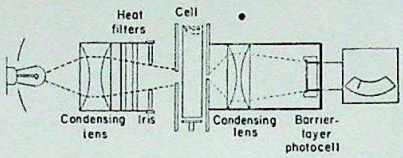


Figure 24. Optical plan of the Wagner Photoelectric Turbidimeter.

active parent element; minimum amount of an organic adsorbate with which a porous packing must be impregnated to permit a supersaturated solution of the impregnant in contact with one end of the packing to be seeded by the introduction of seed crystals at the other end of the packing; trajectories traveled by aerosol particles in an electro-static precipitator; amplitudes of the vibratory motions executed by aerosol particles when subjected to a sonic field of fixed frequency; distance of penetration of suspended particles into a battery of standard, narrow channels (called a "diffusion battery"); forces of adhesion between particles, as measured by the angle of tilt necessary to cause a mass of powder to slide along a surface.

Many of the integral property techniques described in the preceding paragraphs are widely used at present, and as a consequence commercial instrumentation is available for the implementation of these procedures. The following section describes some of this instrumentation that

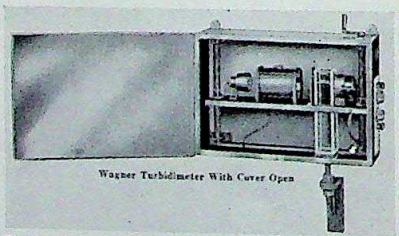


Figure 25. American Instrument Co. version of the Wagner turbidimeter.

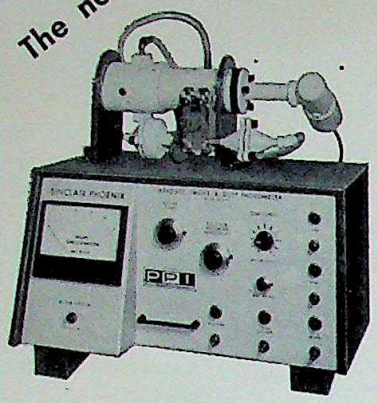
is specifically designed for particle size analysis; other instruments which are primarily designed for other purposes, but which may be applied to particle size determinations, such as, e.g., x-ray diffraction equipment, need not be treated here.

Turbidimeters

A standard turbidimeter for use in the determination of the fineness of Portland

(*Continued on page A434*)

The new



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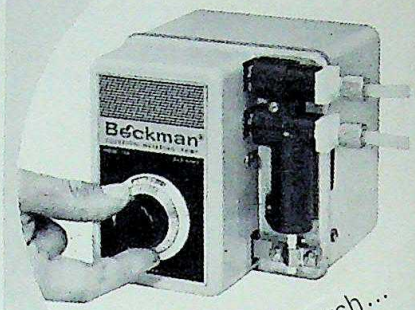
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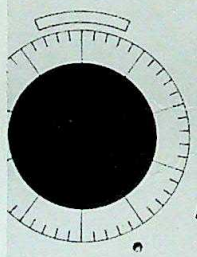
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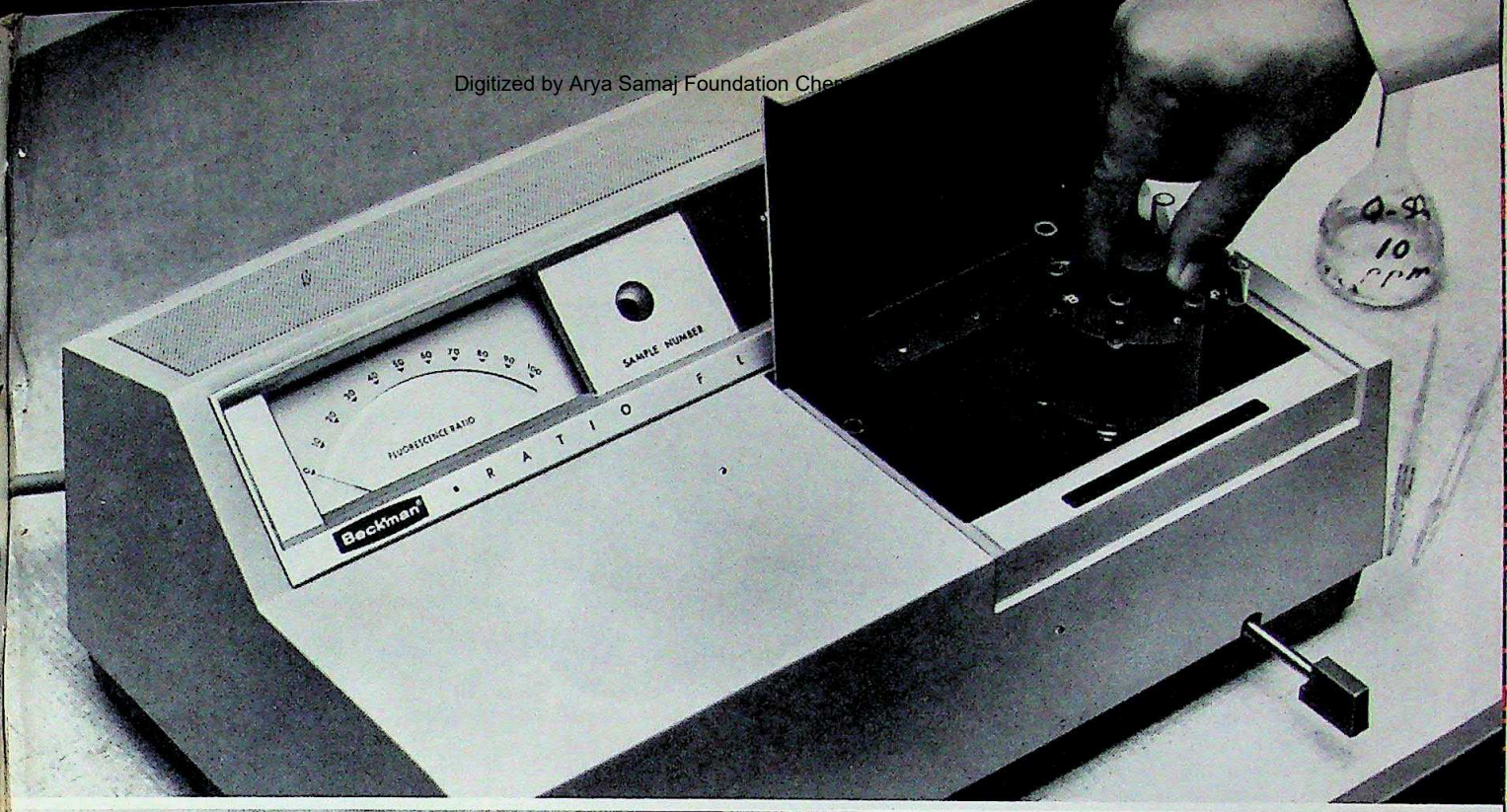
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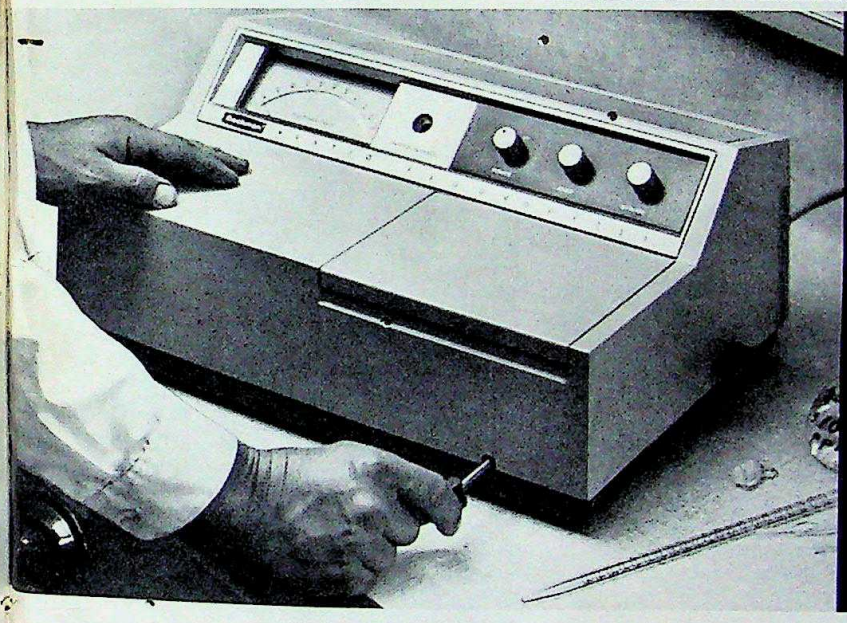
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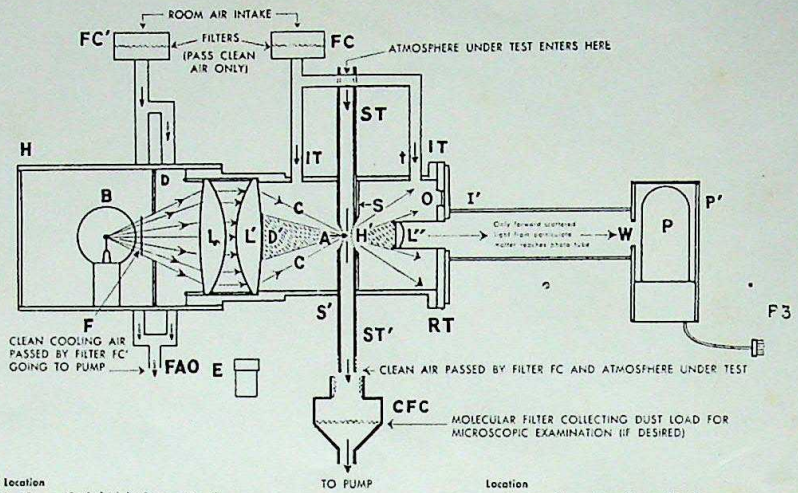
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cements is the Wagner Photoelectric Turbidimeter, shown in diagram in Figure 24 (available from LaPine Scientific Co., Chicago 29, Illinois, $540). It consists of a source of light of constant intensity adjusted so that approximately parallel rays of light pass through a suspension of the substance to be tested and impinge on the surface of a barrier layer photoelectric cell. The transmitted light intensities are measured at various levels in the sample by adjusting the height of the sample cell, and this is done after specified periods of sedimentation in order to yield a particle size distribution. The design of the Wagner turbidimeter made by the American Instrument Co., Silver Spring, Maryland, is shown in Figure 25.

The Phoenix Precision Instrument Co., Philadelphia 40, Pennsylvania, manufactures several instruments based upon the measurement of scattered light. Their Sinclair-Phoenix Forward Scattering Smoke Photometer, shown in Figures 26 and 27, brings the light to a focus at the sample cell, with a diaphragm stop placed in the optical path so that a diverging cone of darkness encompasses the light collecting lens of the photomultiplier

(*Continued on page A440*)



Location
- H — Sealed Light Source Housing
- B — Lamp
- D — Feathered Edge Diaphragm
- L — Condenser Lens
- L' — Condenser Lens
- D' — Diaphragm Stop Produces converging cone of darkness
- IT — Filtered Air Inlets
- FC — Optical System protector filter and carrier
- E — Removable eyepiece which replaces photomultiplier tube for visual observation of smoke particles, also used for alignment
- CFC — Mass collector filter carrier
- A — Stray Light Limiting Diaphragm
- F — Heat Absorbing Filter
- FC' — Light Source System Protector filter and carrier

Location
- C — Converging Cone of Light
- ST — Smoke Inlet Tube
- ST' — Smoke and Filtered Air Outlet Tube
- H' — Diverging Cone of Darkness
- S — Stray Light Diaphragm
- O — Optical Calibration Filters
- L" — Scattered Light Collecting Lens
- I' — Light Trap Tube
- W — Photomultiplier Tube Diaphragm
- P — Photomultiplier Tube
- P' — Shielded Photomultiplier Tube Housing
- S' — Sealed Optical Housing
- P3 — Cable to Logarithmic Amplifier
- FAO — Lamp Filtered Air Outlet
- RT — Rotatable Light Trap Tube Flange

Figure 26. Optical plan of the Sinclair-Phoenix Forward-Scattering Smoke Photometer.

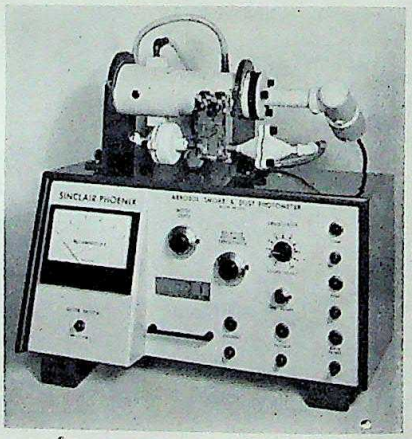


Figure 27. Photograph of Sinclair-Phoenix instrument.

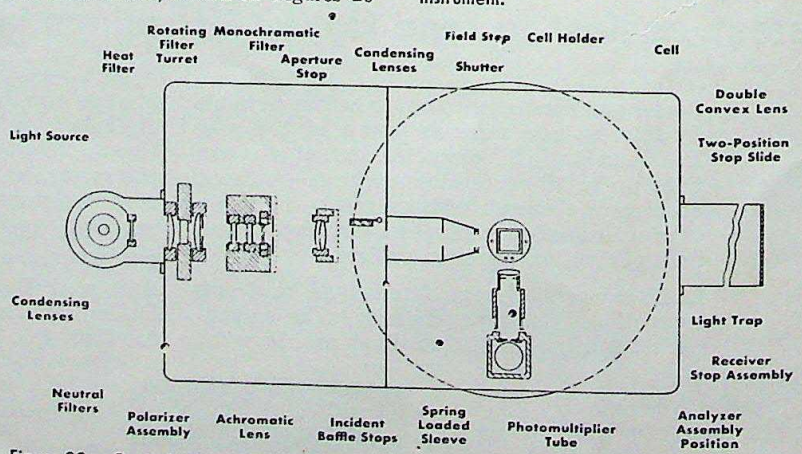
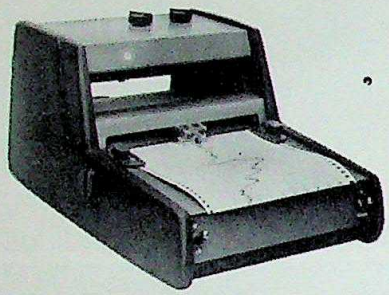


Figure 28. Optical plan of the Aminco Absolute Light Scattering Photometer.

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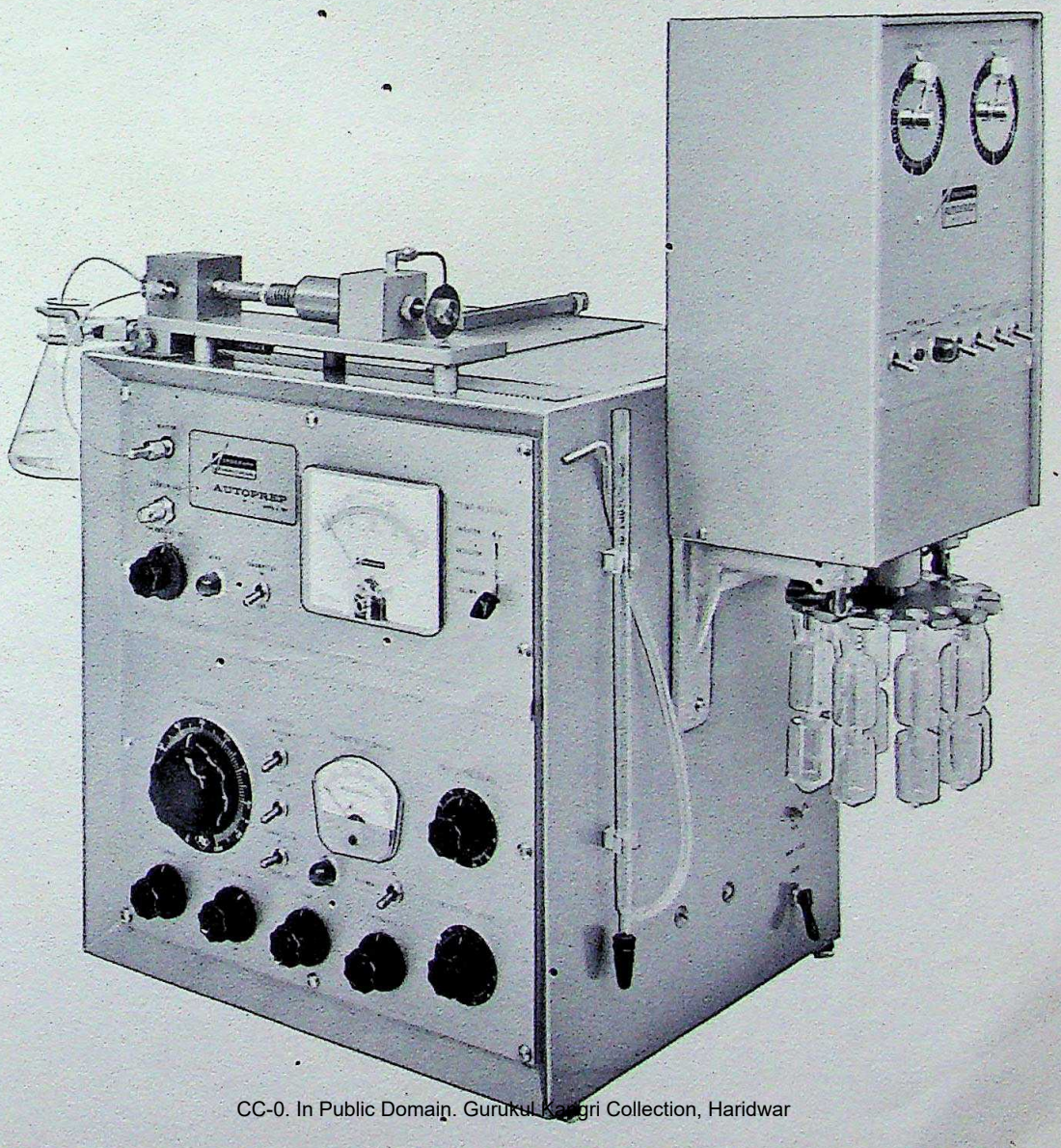
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Price **$400**

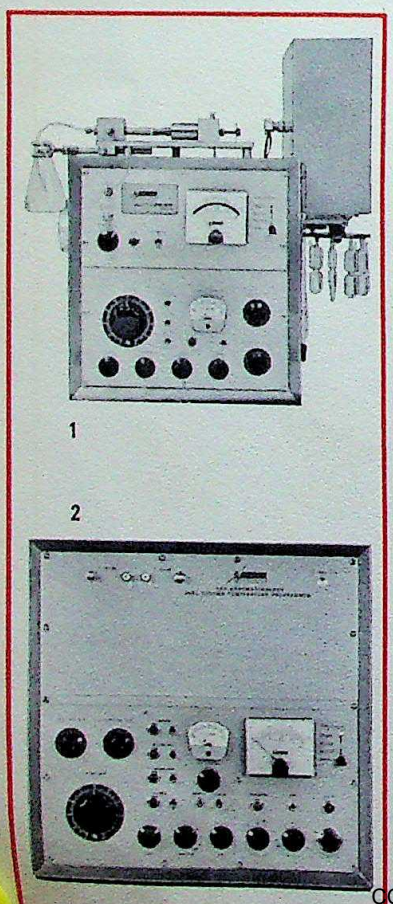
4 AEROGRAPH ELECTROMETER A-500-B
is for Flame Ionization or Electron Capture Detectors; line-operated, features three signal attenuators with a dynamic range of one million, flame ignition button, and fine-coarse zero controls. Price **$575**

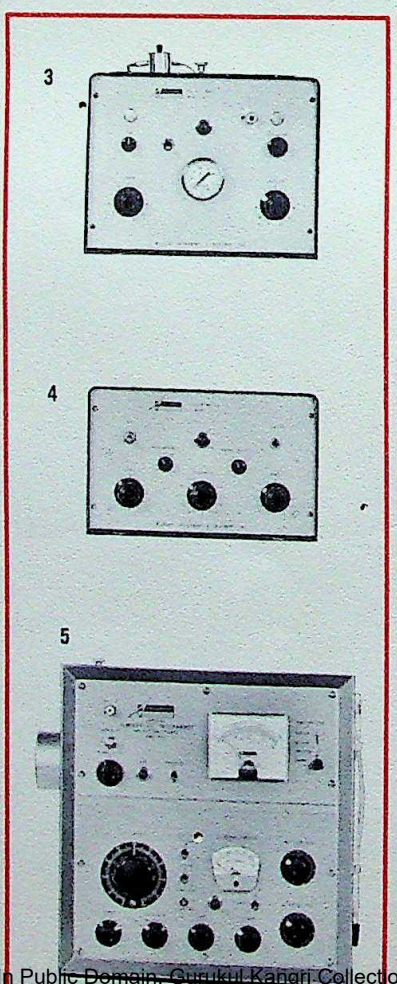
5 AEROGRAPH A-90-P
is a manual temperature programming chromatograph with separate heaters for column oven, detector oven, and injector; with indicating pyrometer, air circulating fan, transistorized power supply. Price **$1095**

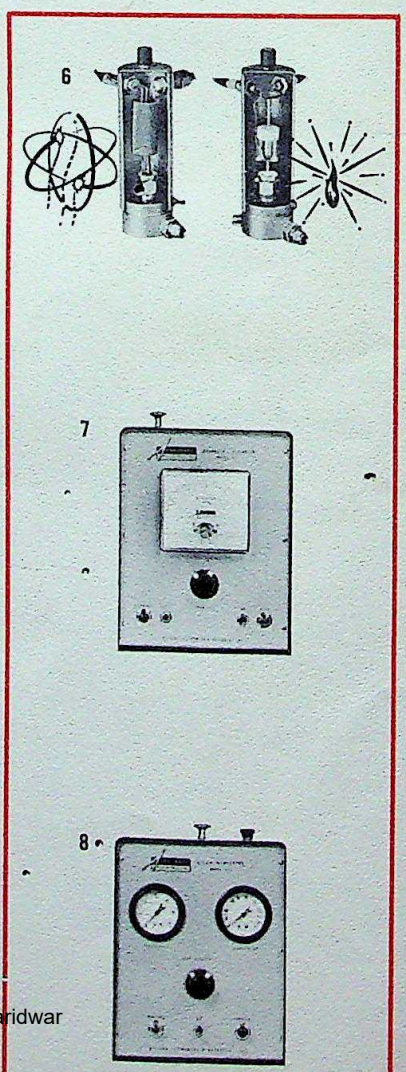
6 AEROGRAPH Hy-FI DETECTORS
are available in Concentric tube Electron Capture Detector, or Hydrogen Flame Ionization Detector. The two outwardly identical heads may be interchanged in minutes. For Aerograph A-600-B Hy-FI and Aerograph A-550-B Oven.

7 AEROGRAPH HYDROGEN GENERATOR
with filtered air supply is complete with meter, controls, plumbing and ⅛" compression fittings for hydrogen and air connections. Especially designed for use with Flame Ionization Detectors. Price **$295**

8 AEROGRAPH STEAM GENERATOR
provides a continuous supply of clean, dry steam for use as a carrier gas for the Aerograph Hy-FI or any gas chromatograph using a Flame Detector. Complete with safety valves, meters, and accessories. Price **$275**







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FOR GAS CHROMATOGRAPHY . . . a complete instrument line and complete, rapid G.C. service.

Wilkens has one special objective . . . to keep you informed and pleased with Aerograph instrumentation. We know that much of our business comes from word of mouth.

Have you talked to an Aerograph user recently?

9 BROWN RECORDERS
are ideal for gas chromatography use, and are compatible with the famous Disc Integrator. Uses capillary pen, zener diode reference supply, and high gain amplifier. Stocked for immediate delivery. Price **$1000**

10 TEMPERATURE PROGRAMMER
controller is complete with platinum resistance thermometer, 0-400°C pyrometer and thermocouple input connections. For programming temperature of a gas chromatograph or any heated instrument. Price **$685**

11 AEROGRAPH POWER SUPPLY
is a line-operated, extremely stable transistorized power supply which will effectively replace wet storage batteries. Will supply 12 or 20 volts at 500 milliamperes. With extra AC outlets on back panel. Price **$150**

12 DETECTOR TRANSFER SWITCH
is used to interconnect two detectors in separate column ovens to a single electrometer and recorder, giving the chemist two complete gas chromatography systems. Shielded, for use with EC or FI Detectors. Price **$55.00**

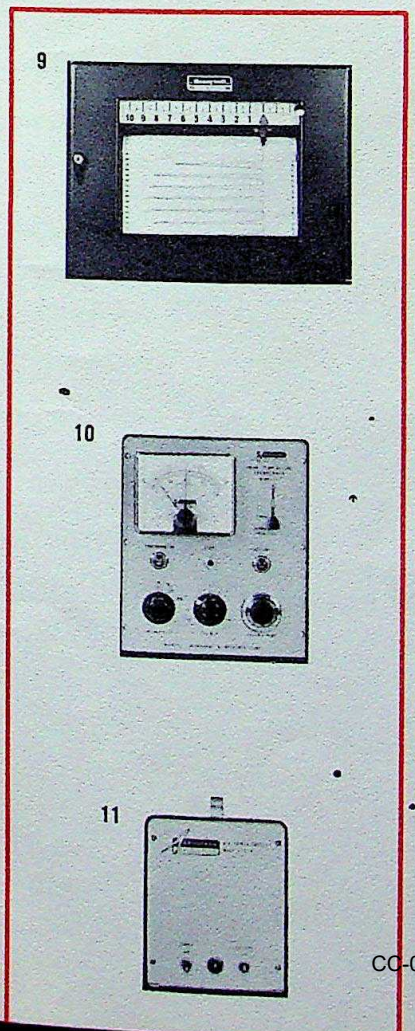
13 AEROGRAPH Hy-FI
is a manual temperature programming gas chromatograph with Hydrogen Flame Ionization detector, or interchangeable Electron Capture Detector. Complete with Hydrogen Flame Ionization Detector Price **$995**
Complete with Concentric Tube Electron Capture Detector Price **$1175**

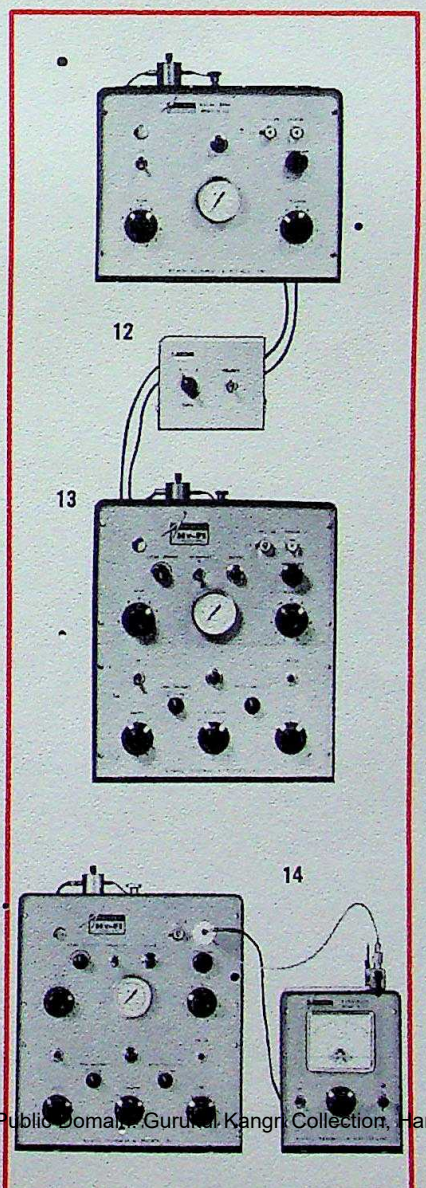
14 AEROGRAPH PYROLYZER
(shown with Aerograph Hy-FI) is used to convert non-volatile substances to characteristic volatile components by thermal fision. Analysis of these volatiles is made by gas chromatography, with flame or electron capture detectors. Price **$250**

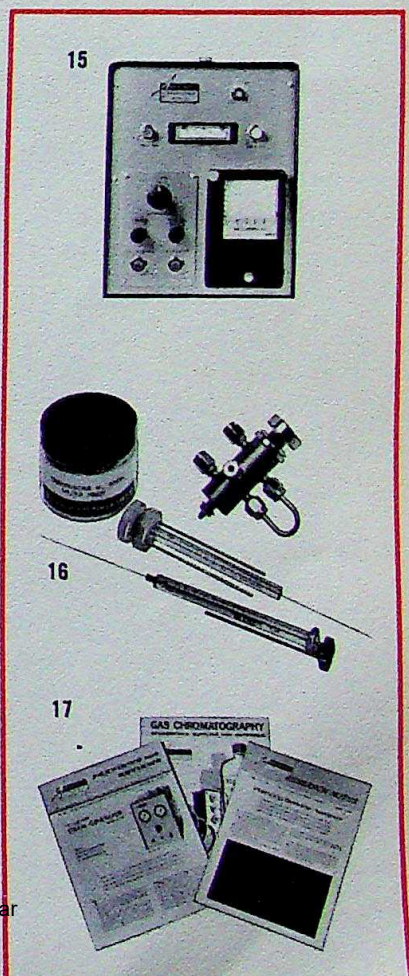
15 NEW AEROGRAPH PESTILYZER
is designed specifically for pesticide residue analysis, and utilizes the unique Aerograph Concentric Tube Electron Capture Detector. Built-in strip chart recorder. Write for Aerograph Pesticide Bulletin. Price **$990**

16 AEROGRAPH ACCESSORIES
A large stock of Hamilton Syringes, Disc Integrators, Aerograph gas sampling valves, columns, packings, and other GC accessories, supplies and materials is kept on hand for immediate delivery. Send for special Accessory catalog.

17 RESEARCH NOTES
Aerograph Research Notes and Previews and Reviews are distributed free to those interested. These publications contain traces, data and results of gas chromatography analysis to help keep the busy chemist current in this rapidly advancing field. If you are not already on our mailing list or if you have a friend or colleague that would like to receive this free subscription, please send name, title, and company address.



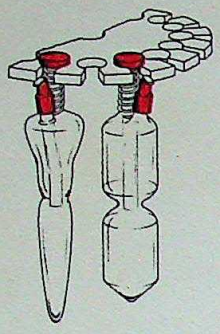


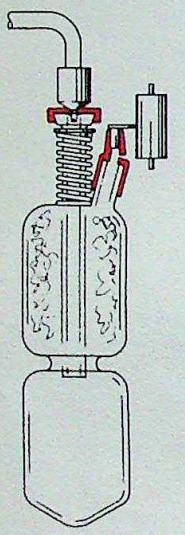


AEROGRAPH FOR GAS CHROMATOGRAPHY

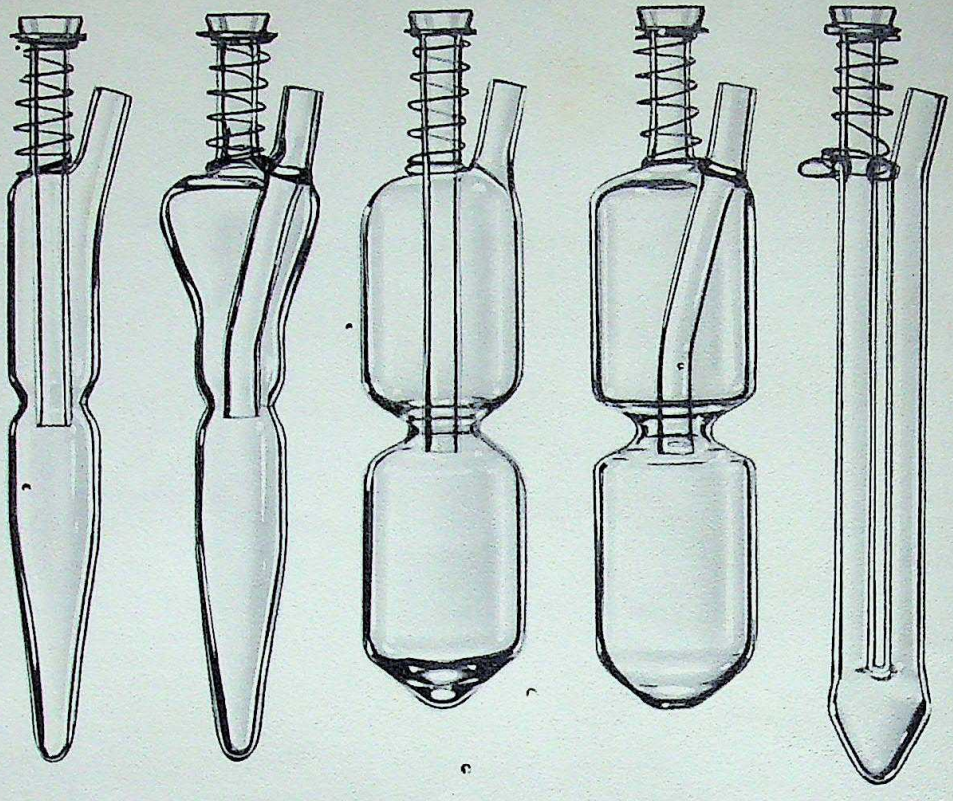
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A



1 2 3 4 5

AEROGRAPH

AUTOPREP COLLECTION BOTTLES

The Autoprep is a completely automatic preparative scale gas chromatograph having a rotating table which carries the sample collection bottles. The efficiency of these bottles has been established with ethyl ether, methyl laurate, and camphor (tabulated below).

Camphor, a sticky solid, is easily collected in gram quantities with bottle types 2 and 4, but will quickly plug types 1, 3 and 5.

The efficient system of bottle closure is shown in Figure A. A positive seal against atmosphere contamination is obtained with a silicone rubber cap and an automatically opened vent valve.

All compounds boiling above 100°C are nearly quantitatively collected without need of cooling. Aerosol-formers are no problem when glass wool scrubbers are used.

We solicit your inquiry on the highly efficient Autoprep. It was built for the chemist who needs to collect gram quantities of ultra pure materials which cannot be separated by conventional distillation.

Bottle	Ether %	Methyl Laurate %	Camphor %
1	90.2	93.0	Plugged
2	81.0	88.5	92.7
3	84.3	90.9	Plugged
4	81.0	84.0	93.3
5	91.3	96.0	Plugged

WILKENS INSTRUMENT & RESEARCH, INC. BOX 313, WALNUT CREEK, CALIF. • PHONE 415-284-7166

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PHARMACIA
LEADING IN DEXTRAN CHEMISTRY

Sephadex® A NEW CONCEPT IN ION EXCHANGERS

DEAE-Sephadex a major development in Ion Exchangers

Introduction of ionic groups into SEPHADEX makes possible ion exchange materials with high capacity and low nonspecific adsorption. SEPHADEX, a hydrophilic insoluble substance, is made by cross-linking the polysaccharide dextran. Both dextran and SEPHADEX were developed by Pharmacia in Uppsala, Sweden.

DEAE-SEPHADEX, containing the active radical diethylaminoethyl, is the first commercially available ion exchanger derived from dextran. DEAE-SEPHADEX is anionic, medium basic, and has a strong affinity for water. The swelling is proportionate to the degree of cross-linkage, the counterions, and ionic composition of the surrounding medium.

DEAE-SEPHADEX has many unique characteristics. Its stability in many mediums — water, weak acids, saline and alkaline solutions — offers many application opportunities. The gel is affected only by strong acids at elevated temperatures and strong oxidizing agents. DEAE-SEPHADEX is especially suitable for labile compounds.

DEAE-SEPHADEX is available in two types with different porosities: A-25 and A-50. A-25 is highly cross-linked and has a high capacity for molecules smaller than 10,000 in molecular weight. Ionic groups in A-50 are accessible to much larger molecules. A-50 has far greater binding capacity than A-25 for the larger molecules. Each has a total exchange capacity 3-4 meq/g.

Illustration of Relative Capacities for Various Proteins

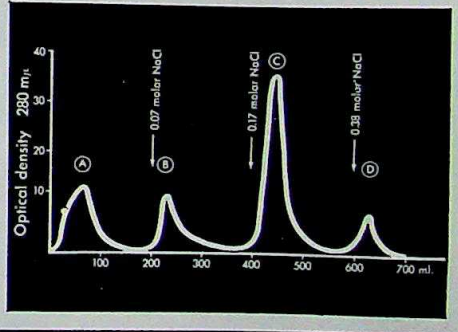
PROTEINS	DEAE-SEPHADEX	
	A-25	A-50
Pepsin at pH 3.6	0.2 g./g.	1.6 g./g.
Amylase at pH 8.3	0.3 g./g.	2.4 g./g.
Ovalbumin at pH 7.6	0.2 g./g.	1.2 g./g.
Hemoglobin at pH 8.8	0.4 g./g.	1.4 g./g.

APPLICATION

DEAE-SEPHADEX may be used in column and batch operations. Chromatographic fractionations are preferably made with Medium and Fine grades. The Coarse grade is more suitable for separations in batches. The particle size of these grades are Coarse (approx. 50-140 mesh), Medium (approx. 100-270 mesh), and Fine (approx. 200-400 mesh).

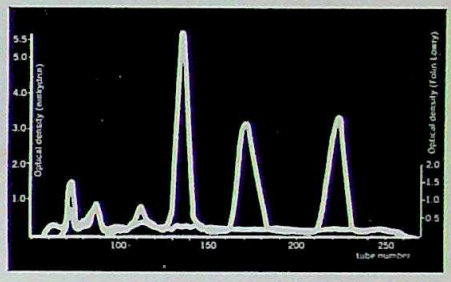
Purification, separation, and fractionation in organic and biochemical research and production processes achieve substantial yields with selection of the proper DEAE-SEPHADEX. A variety of problems in protein chemistry can be solved, e.g., purification of enzymes. Easy fractionations and high yields of serum proteins are possible with DEAE-SEPHADEX A-50. This is illustrated by Figure I.

Separation of Normal Human Serum
Fig. I



Nucleic acids, nucleotides, and a wide range of oligonucleotides can be readily bound and separated by fractional elution. Separation of polypeptide mixtures is possible by fractionating through ion exchange and ion exclusion. This is exemplified by Figure II.

Fractionation of Pituitary Hormones
Fig. II



TWO CATION EXCHANGERS AVAILABLE

For separation and fractionation of complex organic substances and protein groups, Pharmacia has developed two new cationic SEPHADEX compounds which are dextran derivatives. Sulfoethyl is the active group for SE-SEPHADEX and is strongly acidic. The active radical for the weakly acidic CM-SEPHADEX is carboxymethyl.

SE-SEPHADEX and CM-SEPHADEX are prepared in two forms. C-25, which is ideal for separating low molecular weight complex organic substances, and C-50, which has proved very satisfactory for purification of proteins, enzymes, and related nitrogenous compounds.

SE-SEPHADEX and CM-SEPHADEX cover a broad range in total exchange capacity, 2-2.5 meq/g and 4-5 meq/g respectively. Both products are available in the following sieve fractions: Coarse (approx. 50-140 mesh), Medium (approx. 100-270 mesh), and Fine (approx. 200-400 mesh).

For complete information including latest developments on SEPHADEX *and* ION EXCHANGERS, *send the coupon with your letterhead.*

PHARMACIA FINE CHEMICALS, INC.
501 Fifth Avenue, New York 17, New York
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☐ Please send me technical information on SEPHADEX Ion Exchangers

☐ Please send me, regularly, Ion Exchanger abstracts

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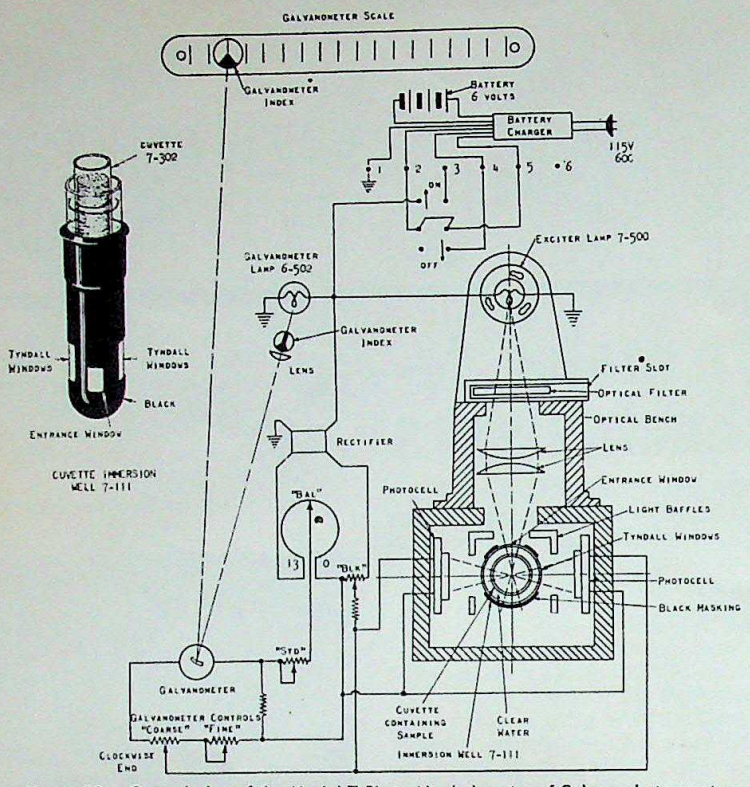


Figure 29. Optical plan of the Model 7 Photo-Nephelometer of Coleman Instruments.

housing. Hence, the only light reaching the detector is that which is scattered in the forward direction by the specimen. This results in a high sensitivity to particulates in the sample stream; calibration with a dioctyl phthalate oil fog of 0.3 micron droplet diameter indicates 10^{-3} micrograms per liter as the minimum detectable concentration of aerosol.

This company also makes a light-scattering photometer designed for the measurement of the types of scattered intensities needed in the determination of the molecular weights of macromolecules by the Debye technique. The instrument, known as the Brice-Phoenix Light Scattering Photometer, may also be utilized for fluorescence, transmittance, and reflectance measurements. It consists essentially of an optical bench, light source, photomultiplier detector, sample compartment, and associated electronics.

The American Instrument Co. offers a similar instrument as their Absolute Light Scattering Photometer ($2900). The optical plan of this instrument is shown in Figure 28.

The Model 7 Photo-Nephelometer of Coleman Instruments, Inc., Maywood, Illinois, shown in Figure 29, is designed for precise analytical work with turbid solutions. There are two photocells, viewing the light scattered at 90° to the incident direction. The summed output is read out by means of a sensitive galvanometer. Another instrument is available, viz., the Model 9 Nepho-Colorimeter, which incorporates a third photocell in line with the transmitted beam, so that the device can be employed either for transmittance or scattering measurements.

A recording turbidimeter, designed for use in the continuous monitoring of a flowing liquid stream, is made by General Electric Co., Schenectady, New York.

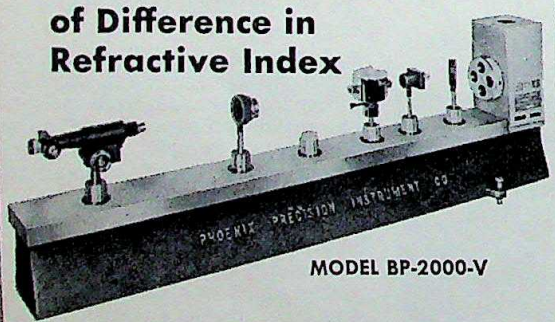
Permeameters

Several instruments based upon the

(*Continued on page A442*)

PPI

Direct Measurement of Difference in Refractive Index



MODEL BP-2000-V

The New Brice-Phoenix Differential Refractometer uses a split cell to measure the difference in refractive index between a dilute solution and its solvent.

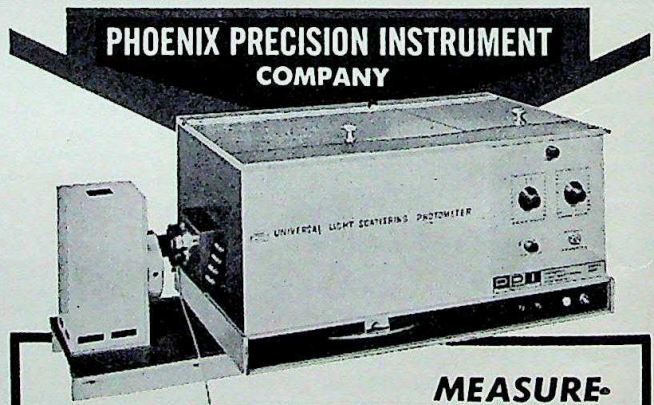
Sensitivity 3 x 10^{-6}.

For complete details write Dept. CE-3

PHOENIX PRECISION INSTRUMENT COMPANY

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PHOENIX PRECISION INSTRUMENT COMPANY



MEASURE- MOLECULAR WEIGHT AND PARTICLE SIZE

NEW BRICE-PHOENIX UNIVERSAL LIGHT SCATTERING PHOTOMETER
MODEL 2000

Measures:

1. Absolute Turbidity 2. Dissymmetry 3. Depolarization

This instrument is listed in U.S. Government specifications for the evaluation of certain clinical materials.

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PPI

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Mettler

METTLER H-6 SPECIFICATIONS

PERFORMANCE DATA	
Capacity	160 g
Optical Scale Range	1200 mg
Sensitivity (1 micrometer graduation)	0.1 mg
Readability (1 micrometer graduation)	0.1 mg
Accuracy of weight set	± 0.1 mg
Accuracy of weighings within optical range	± 0.1 mg
Precision	± 0.05 mg
DESIGN DATA	
Damping	differential, top and bottom air damping
Knife edges and planes	synthetic sapphire
Taring range (up to)	15 g
Pan:	chrome-nickel steel
diameter	3½"
bracket height	6½"
Weights, annular	non-magnetic chrome-nickel steel
*Density	7.77 g/cm^3
Housing	plastic, two colored
Base Plate	light alloy
Dimensions: width	8-3/4"
depth	14"
height	15½"
Voltages	4 settings, from 110 to 220 V AC, set for 110
Net weight	17.5 lbs
Shipping Weight	24 lbs

ACCESSORIES: Adaptor, Screwdriver, Dust brush, Cleaning cloth, Dust cover, Spare bulb.

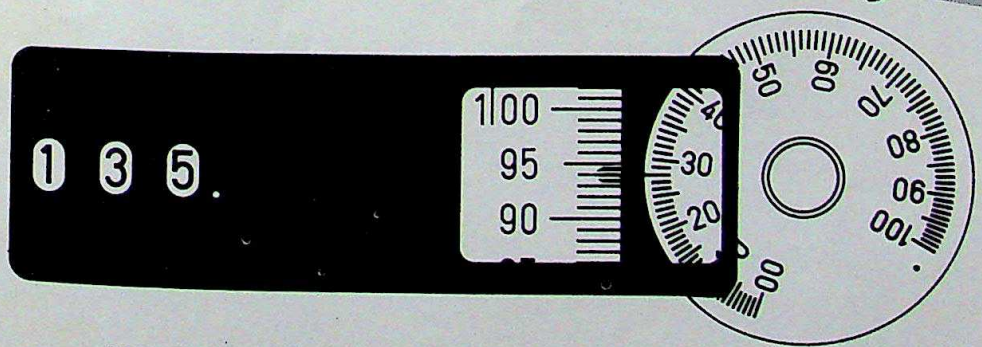
*) at air-density 1200 mg/l calibrated to apparent mass of density 8.4 g/cm^3.

HAVE YOU SEEN THE NEW METTLER H-6 !
1200 mg optical range
100 scale division micrometer
.05 mg precision—
and only $670 !

H-6



H-6 Readout showing hundred scale division micrometer (actual size)



Mettler Instrument Corp. - 20 Nassau Street - Princeton, N. J.

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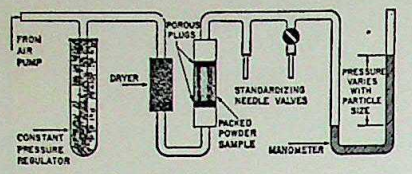


Figure 30. The Sub-Sieve Sizer, an air permeability apparatus made by Fisher Scientific Co.

measurement of the air permeability of a compacted powder or porous solid specimen are in current use. The Sub-Sieve Sizer made by Fisher Scientific Co., Pittsburgh 19, Pennsylvania ($465) is illustrated in Figure 30. A regulated flow of dry air is passed through a weighed sample packed under strictly standardized conditions into a special cell, and the pressure on the outlet side of the packing is measured. Calibration charts are available for converting the manometer reading to average particle size.

A simpler, less precise instrument that is based upon the same principle is the Precision-Blaine Fineness Tester (available from most laboratory supply houses, about $100). It consists of a manometer, test cell, and stopcock-rubber aspirator bulb assembly for creating the air flow.

Gas Adsorption Instrumentation

The Numec Instruments and Controls Corp., Apollo, Pennsylvania, manufactures several instruments for the determination of surface areas and pore volumes by means of the principles involved in low temperature gas adsorption. Their Adsorption Flow Apparatus ($1795) employs a slow, constant flow of nitrogen gas into the sample until a preselected equilibrium pressure has been attained, at which point the flow stops and the volume of gas adsorbed is determined. This permits data to be obtained very rapidly and conveniently. For more precision, BET data can be obtained by standard volumetric measurements at several gas pressures. The instrument is shown in Figure 31.

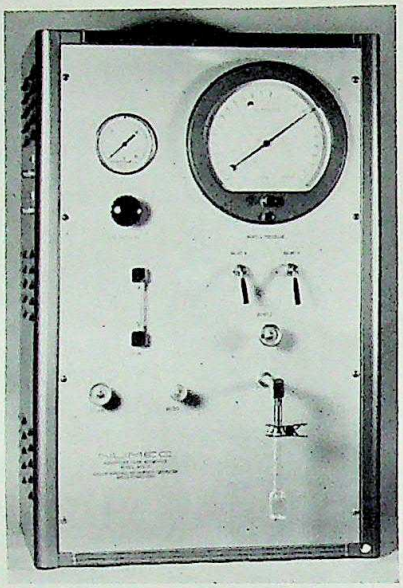


Figure 31. The Numec Adsorption Flow Apparatus.

A more sophisticated device for facilitating BET gas adsorption measurements is the Numinco-Orr Surface Area-Pore Volume Analyzer ($6700) from the same company. It incorporates a seven-valve manifold which interconnects three sample holders, an evacuation system consisting of a cold trap, oil diffusion pump and mechanical pump, a variable volume space, pressure indicators, gas inlets, a timer, a thermistor thermometer, and electrical switching controls.

Gas chromatographic instrumentation has been applied to the problem of determining quantities of adsorbed nitrogen and other gases in the Model 212 Sorptometer made by Perkin-Elmer Corp., Norwalk, Connecticut ($1750, without recorder). The schematic diagram is shown in Figure 32. A mixture of helium and

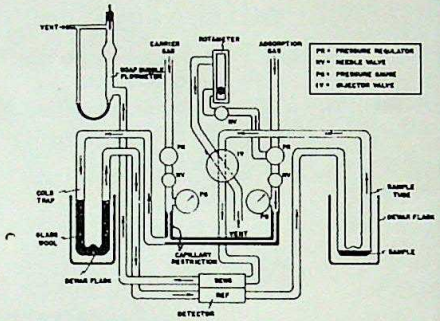


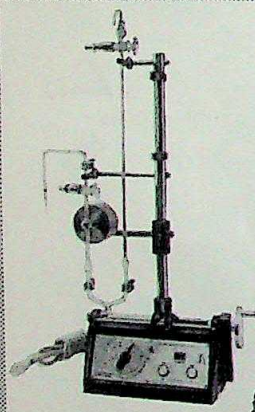
Figure 32. Flow schematic of the Model 212 Perkin-Elmer-Shell Sorptometer.

(*Continued on page A444*)

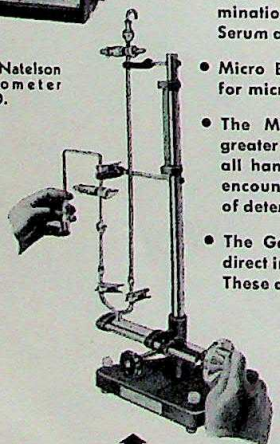
the NATELSON
MICROGASOMETERS
for Gas Determinations of Ultra-Micro Samples

EASY TO LEARN! Natelson Microgasometers adapt the classical Van Slyke manometric method to ultra micro analysis. Improvements in technique, sampling, accuracy and ease of operation have been developed while achieving this adaptation.

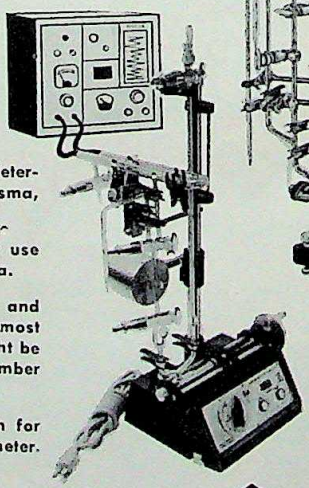
- 0.03 ml. sample provides accurate quantitative determinations of CO_2—O_2—CO—N_2 in Blood, Plasma, Serum and Ammonia.
- Micro Burette attachment enables Microgasometer use for micro titrations such as Chlorides and Ammonia.
- The Motorized Microgasometer features speed and greater reproducibility of results by eliminating almost all hand manipulation and the fatigue which might be encountered in continual operation when a great number of determinations are to be run.
- The Gas Injector attachment provides the system for direct injection of gases liberated in the Microgasometer. These are fed into a Gas Chromatograph.



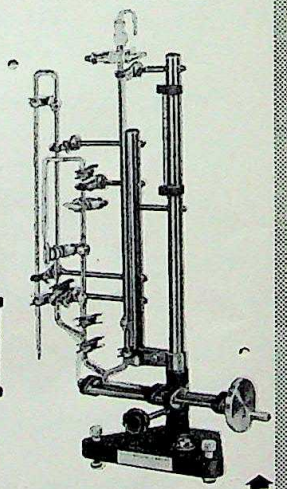
Motorized Natelson Microgasometer Model #650.



Natelson Microgasometer Model #600.



Motorized Natelson Microgasometer Model #650 shown with Gas Injector attachment #M-373-25 as it would be utilized with any Gas Chromatograph apparatus.



Natelson Microgasometer Model #600 shown with Micro Burette attachment #M-373-12.

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performance-proved instruments
for SPECTROSCOPY

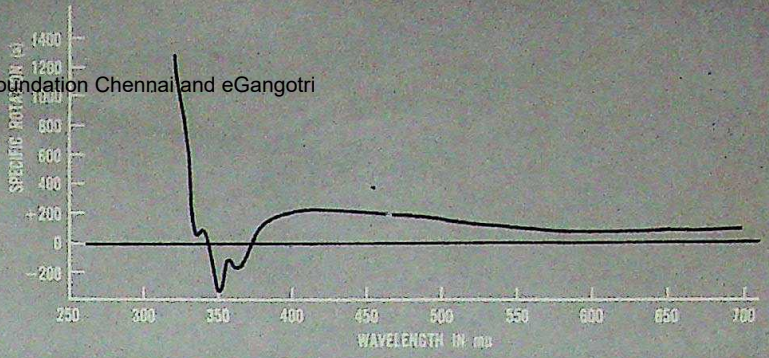


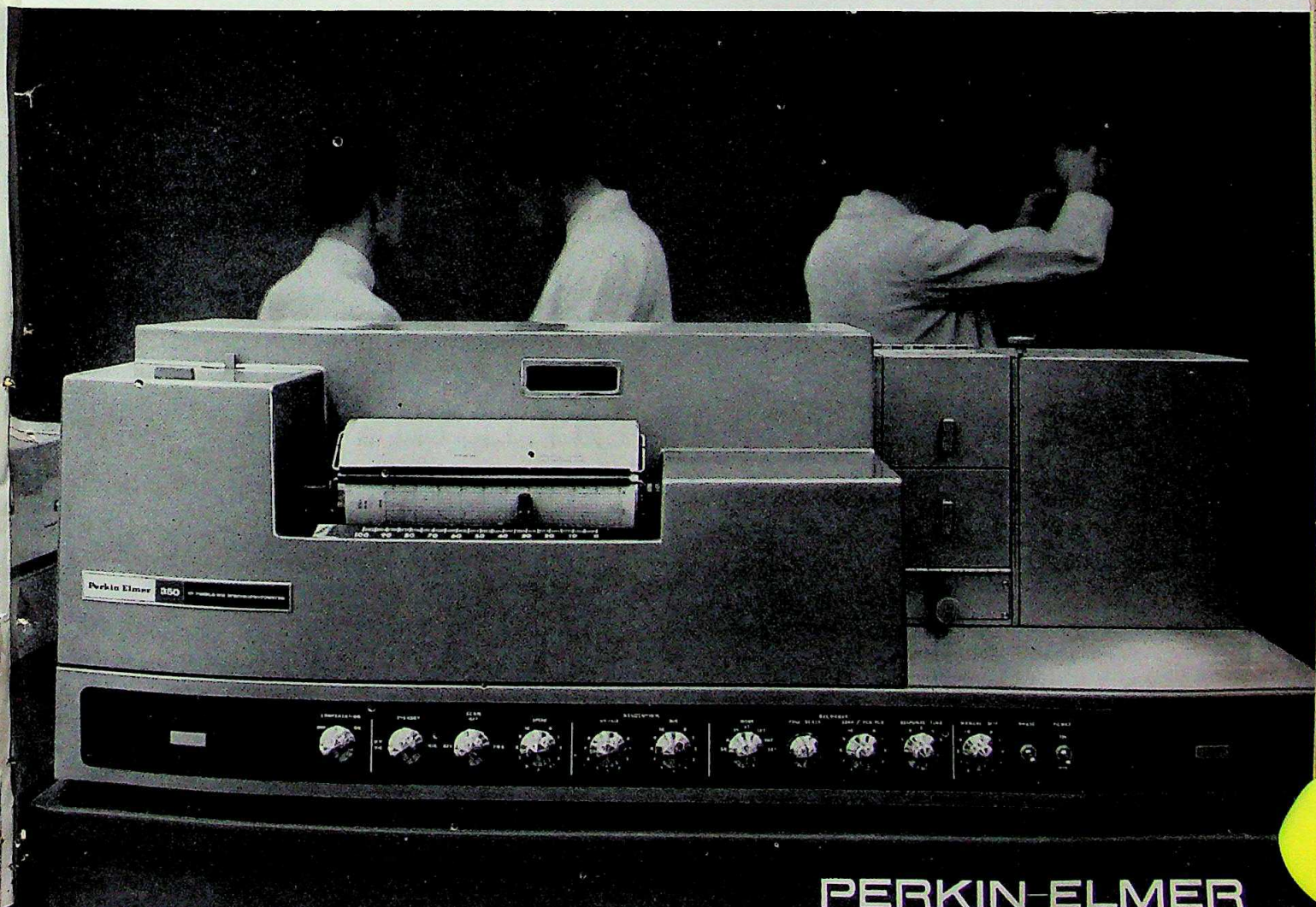
Chart shows spectral analysis by Optical Rotatory Dispersion of 2mg of testosterone in p-dioxane. With identical calcite polarizer-analyzer combinations in each beam, absorption by the sample is canceled out. Rotation of the light by the sample appears as a pen deflection on the chart, whence it is readily convertible to angular units by conversion tables provided with the accessory. The high scale expansions available on the Model 350 can be used to advantage in ORD work.

NO OTHER SPECTROPHOTOMETER HAS EQUAL CAPABILITIES THROUGHOUT THE FAR-ULTRAVIOLET TO NEAR INFRARED RANGE

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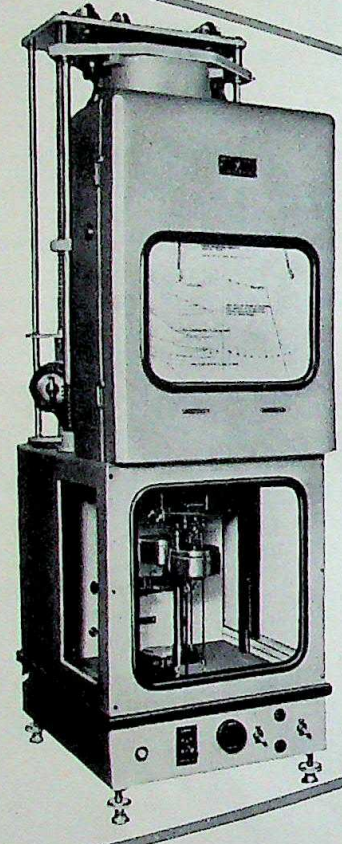
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nitrogen is passed through the sample, and the thermal conductivity is monitored by thermal conductivity detectors placed before and after the sample, as in gas chromatography. When the sample is immersed in liquid nitrogen and is adsorbing nitrogen from the gas stream, the recorder pen is driven downscale by the imbalance in the T/C detector signals. When the adsorption ceases, the recorder pen returns to its base line. Hence, the area of the recorded peak is proportional to the volume of nitrogen removed by adsorption from the gas stream. Similarly, the volume desorbed as the sample is allowed to warm up is recorded as a peak of opposite direction on the recorder. If these measurements are repeated for different He/N_2 ratios of the gas stream, the complete adsorption isotherm can be obtained.

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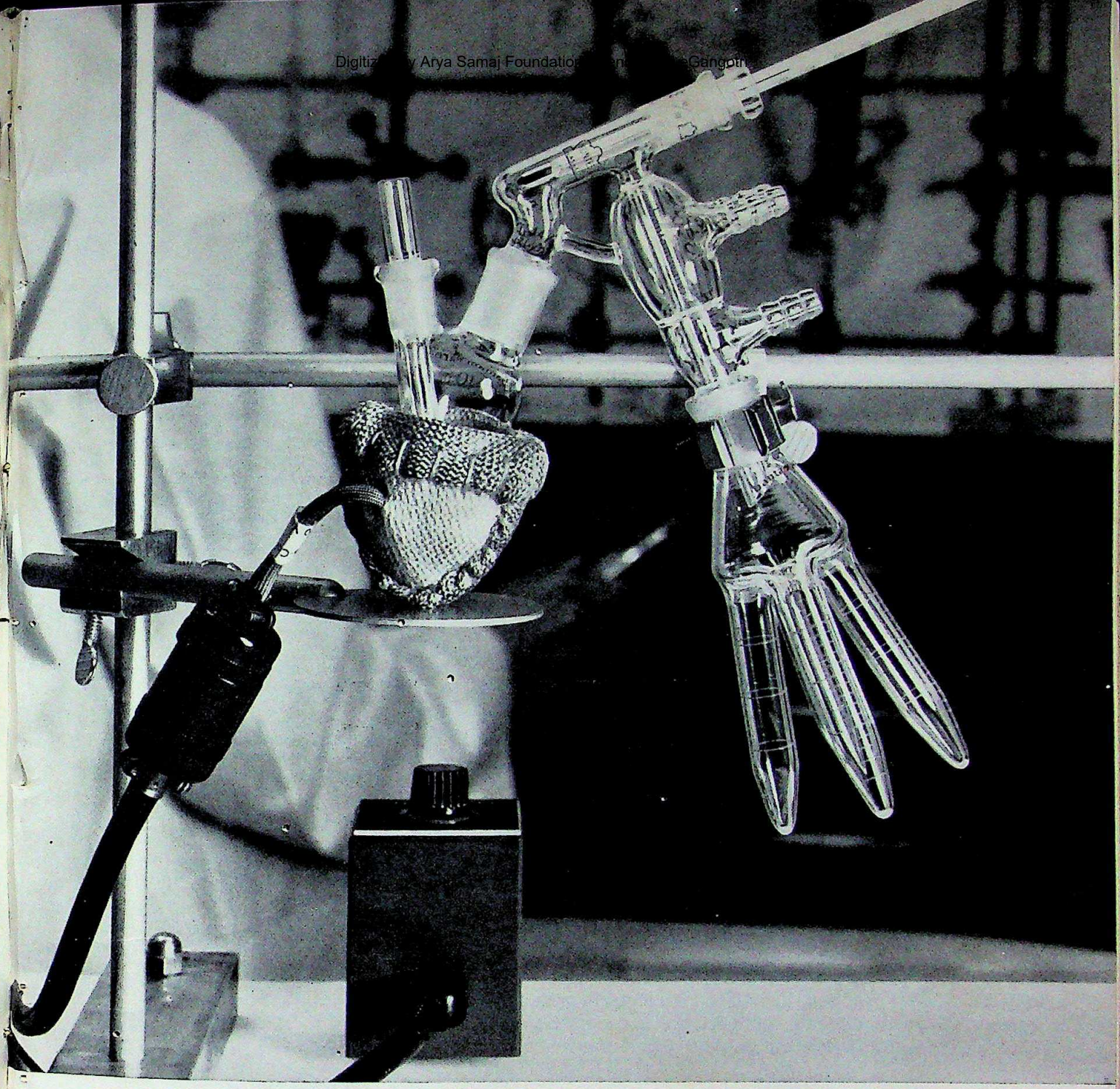
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(*Continued on page A446*)

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Acting on a tip from Dr. Raymond Firestone at Merck & Co., Rahway, we went to work on our new K-28480 Bantam-ware Short Path Fractionator. Make the column about an inch long and let the thermometer bulb and stem serve as a packing, he said. Construct the condenser and vacuum connection in two inches, total length. Use only one joint on the fraction cutter but design it so that pipettes can be inserted to the bottom of any of the four receivers. Then, tilt the whole assembly so that drops fall from the drip tip ₹ 14/20 joint into one of the four receivers without unnecessary wetting. But nothing is vertically aligned, we pleaded. I know, he said. In desperation, we tried it.

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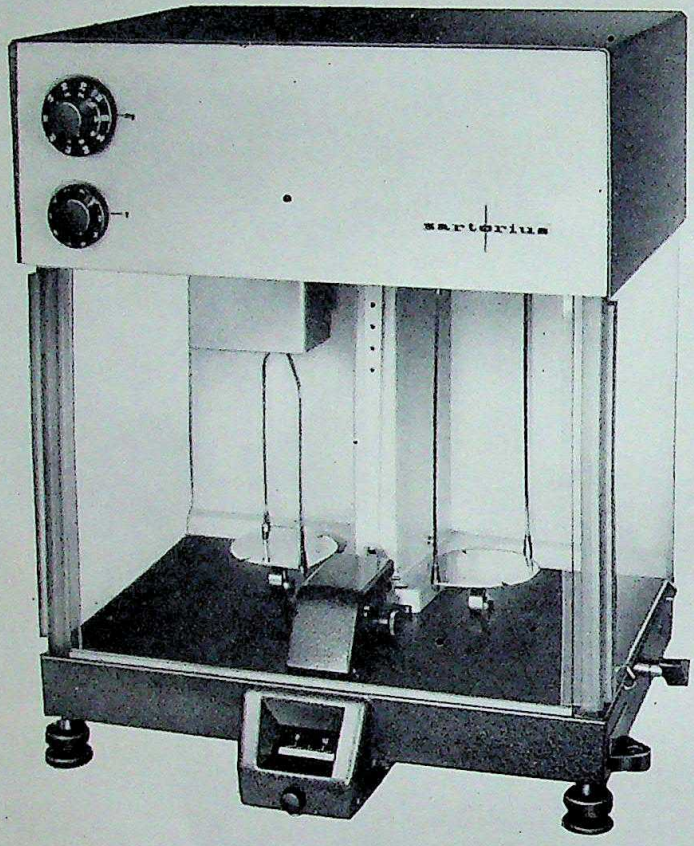
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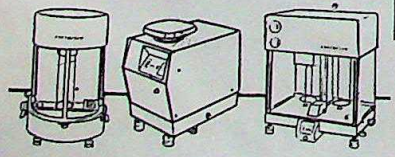


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Out of the EDITOR'S BASKET

Edited by William G. Kessel

When writing for additional information about new products or for new literature, your inquiry will receive prompt attention if you write on your firm or Institution letterhead and mention the Journal of Chemical Education and the date of the particular issue. Pamphlets, booklets and similar literature are gratis unless otherwise specified.

New Apparatus and Equipment

▶ A repeating dispenser syringe attachment is now offered by Hamilton Co., P.O. Box 307, Dept. 272, Whittier, California, for exact repetition of precision droplets. This syringe holder was developed in answer to many requests and has undergone exhaustive research over a considerable period of time.

▶ Nuclear-Chicago Corp., 359 E. Howard Ave. at Nuclear Dr., Des Plaines, Illinois, offers; Model 9100, an instrument calibrated to measure neutrons with energies ranging from 500 kev to 15 Mev. It is designed for use with accelerators, reactors, or for any experimentation which requires a fast neutron measurement with high directionality. The efficiency of the 9100 is two times greater than conventional long counters because it uses a 2 atm Texlium detector, rather than a BF_3 detector included in the original Hanson-McKibben design.

▶ Another Nuclear-Chicago instrument now available is Model 6010 Dynacon, a dynamic capacitor electrometer which is capable of measuring currents as low as 5×10^{-17} ampere and charges in the region of 5×10^{-16} coulomb, with $\pm 1\%$ overall precision for currents of 10^{-15} ampere. It offers a response speed of 0.25 second, along with excellent stability and a high degree of reproducibility.

▶ Scientific Glass Apparatus Co., Inc., Bloomfield, New Jersey, announces an improvement in the design of their Bennert-type differential vacuum gauge which has a range of 0–240 mm in 1 mm divisions.

▶ The Keithley Model 121 wideband true rms voltmeter is said to be the only instrument available for the measurement of complex ac voltages from 15 cps to 50 megacycles. Between 20 cps and 10 megacycles its accuracy is within 1%. Crest factors (ratio of peak value to rms value) of 6 at full-scale and 60 at one-tenth scale deflection assure specified accuracies throughout the entire bandpass. Write Keithley Instruments, 12415 Euclid Ave., Cleveland 6, Ohio, for details.

▶ Bel-Art Products of Pequannock, New Jersey, announces the availability of a full line of red vinyl stoppers which have many advantages over stoppers made from other materials.

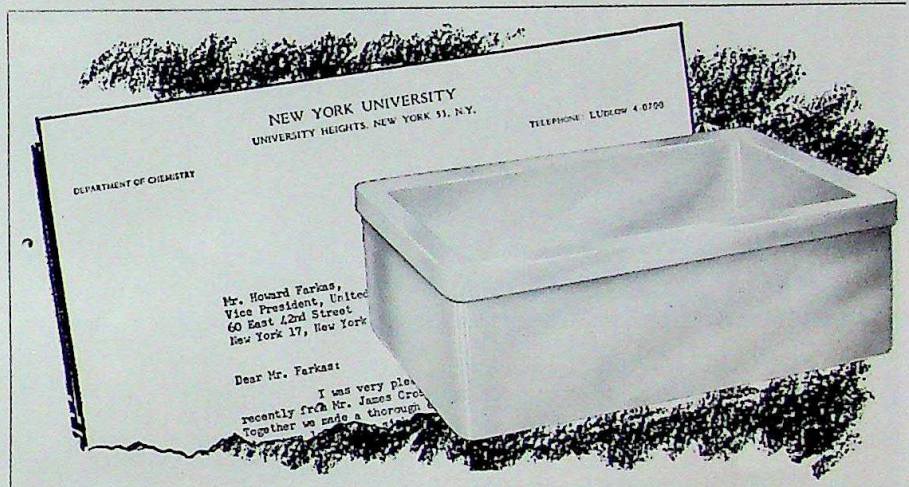
▶ A new automatic low cost liquid level controller and transfer timer is in production at Sulfrian Cryogenics, Inc., Hillside, New Jersey. The device consists of an over-riding automatic recycling timer, a sensor and a probe. These work in conjunction with a Sulfrian solenoid-activated container discharge device and together they permit unattended monitoring and control of liquid nitrogen and liquid oxygen levels in cold traps, research dewars, cryostats, etc.

▶ Technilab Instruments, 2231 S. Carmelina Ave., Los Angeles 64, California, offer a new photometric analyzer, designed to save time, reduce computation errors, and furnish a permanent chart record. The instrument can be used by any laboratory personnel with but a minimum of training.

▶ 1401 S. Post Oak Rd., Houston 27, Texas, home of Infotronics Corp., has introduced a new all-transistorized printing electronic digital integrator for use in gas chromatography and other analytical techniques. This integrator, the CRS-10, is outstanding because of its low cost and functional capacity.

▶ Technical Measurement Corp., 441 Washington Ave., North Haven, Connec-

(*Continued on page A448*)



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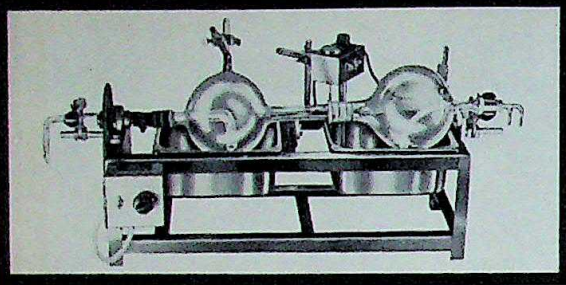
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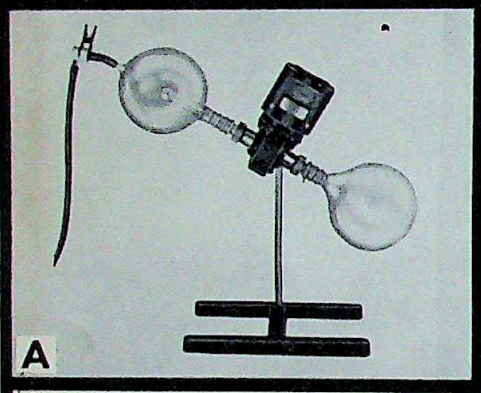
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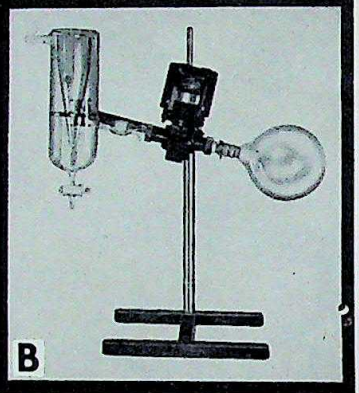
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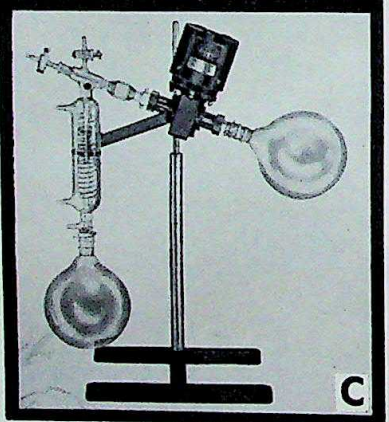
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▶ Phoenix Precision Instrument Co., 3803–05 N. Fifth St., Philadelphia 40, Pennsylvania, announces the availability of a new reusable device for vacuum hydrolysis, a unique apparatus that is useful for the hydrolysis of proteins and other polymeric materials, in an inert atmosphere. Tested under laboratory conditions, this tube withstood 110°C for 48 hr, with no loss of vacuum.

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▶ A new type of laboratory surface equipment affording superior corrosion resistance has been introduced by Polycone Corp., 8858 W. 47th St., P.O. Box 87, La Grange, Illinois. The new line, offered in a full range of sinks, tops, fume hoods and accessories, features an entirely new type of built-up surface material designated as "Resistal."

▶ A new, lightweight, low-cost viewer by A/V Industrial Division of Hudson Photographic Industries, Inc., Irvington-on-Hudson, New York, called the HPI Transparency Comparator provides an ideal source of illumination, and a flat, firm working surface for the construction of overhead projection transparencies. The snap-in face plate, large enough to accommodate 11 in. × 14 in. mounts, features clips to hold the material firmly in place while it is being worked on. When the face plate is reversed, the clips become registration pins for constructing sequence overlays. Further information may be secured by contacting the A/V Industrial Division of Hudson Photographic Industries, Inc.

▶ A precise method of atomic absorption analysis has been instrumented on a practical basis by the Perkin-Elmer Corp., Norwalk, Connecticut. The instrument, designated the Perkin-Elmer Model 303 atomic absorption spectrophotometer, will bring simplicity and speed to routine analyses that once were laborious and to those previously barred due to the high cost of other precise techniques.

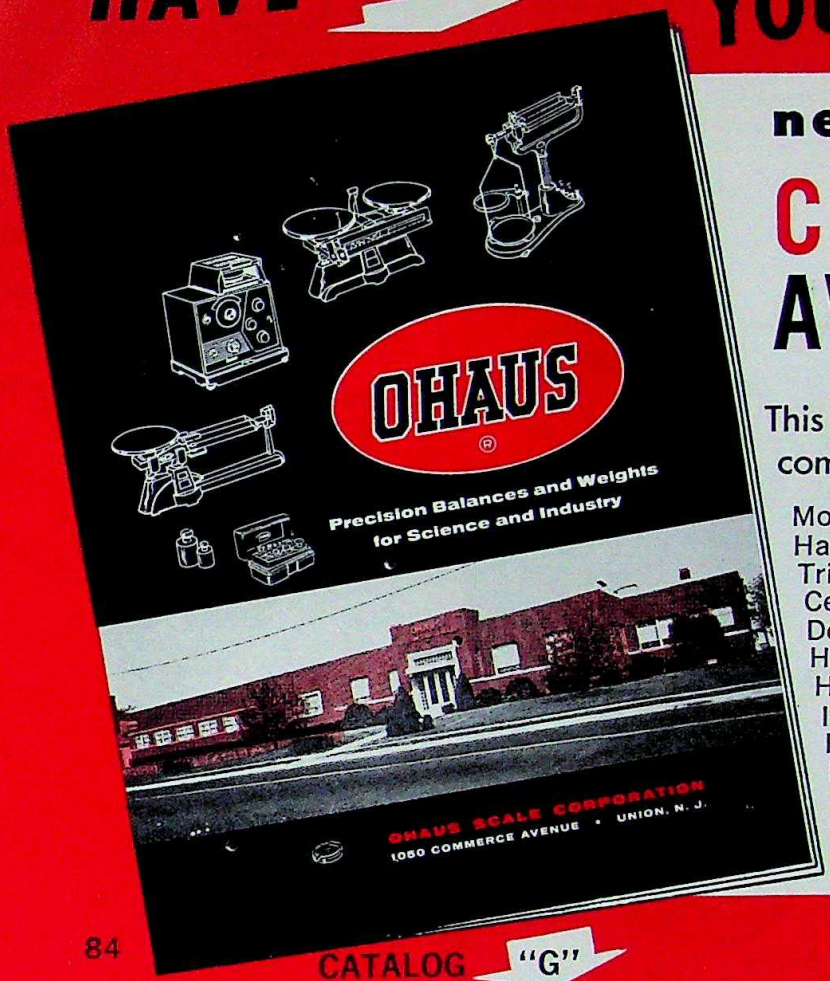
▶ Carl Zeiss, Inc., 444 Fifth Ave., New York 18, N. Y., announces the availability of the Carl Zeiss spectrophotometer PMQ

(*Continued on page A450*)

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▶ Stanley Scientific Glass, Inc., Dept.T., Tullytown, Pennsylvania, producers of all types of scientific glassware, are delivering high-vacuum graded glass-to-sapphire seals to customer specifications.

▶ A new line of self-powered, electronic thermometers, using thermistor probes, has been developed by Atkins Technical Inc., Box 3617, University Station, Gainesville, Florida. These new thermometers, which are a part of an interrelated group of instruments for indicating, recording and controlling temperature, operate within the range of from −153 to +577°F or −102 to +302°C.

▶ A new, compact adjustable-zero, adjustable-range self-balancing potentiometer recorder has been announced by Leeds and Northrup Co., 4901 Stenton Ave., Philadelphia 44, Pennsylvania.

New Literature

● Technical Measurement Corp., 441 Washington Ave., North Haven, Connecticut, has prepared a comprehensive *Conversion Factors* booklet, pocket size, available free on request. The booklet is arranged in three columns headed "To convert" — "Into" — "Multiply by." Every conceivable unit of measurement from converting Angstrom units into inches to watt-hours into ergs are alphabetically listed. Humorous sayings intersperse the copy.

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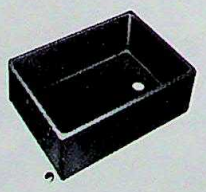
● The Sargent power borer—a machine that bores smooth, uniform holes in corks and stoppers in just seconds—is described and illustrated in *Bulletin PB-1.* A copy is now available from the designer and manufacturer, E. H. Sargent and Co., 4647 W. Foster Ave., Chicago 30, Illinois.

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● Ivan Sorvall, Inc., Norwalk, Connecticut, designers and manufacturers of superspeed centrifuges and laboratory instruments, have just issued a new 20-page, 2-color *Product Guide* that illustrates and describes the complete "Servall" line.

● The publication *High Purity Rare Gases*, prices, specifications, and information is available from Rare Gas Sales Office, Linde Co., 270 Park Ave., New York 17, N. Y.

● LaPine Scientific Co., 6001 S. Knox Ave., Chicago 24, Illinois, has just published the 1963–64 edition of its 192-page catalogue of science equipment for schools. Extensively revised, this new edition introduces many new pieces of science equipment—some listed for the first time in any publication.

● A completely revised, comprehensive bibliography of the literature on "G-4" (Dichlorophene) has just been published by Sindar Corp., 321 W. 44th, New York 36, N. Y. The 27-page bibliography, designated as *Technical Bulletin D-2*, contains references and abstracts on 150 scientific and trade articles, and abstracts of 25 patents.

● A new booklet is available which gives comprehensive technical information on the metal ruthenium and has been published by The International Nickel Co., Inc., 67 Wall St., New York 5, N. Y. This metal which has long been used as a hardener for platinum and palladium, is currently receiving considerable attention as an alloying agent for refractory metals and as a catalyst.

● Copies of the new *1963 Educational Catalog* are available by writing to Central Scientific Co., a division of Cenco Instruments Corp., 1700 W. Irving Park Rd., Chicago 13, Illinois.

● Purification of water for use in the laboratory is discussed in the March 1963 issue (No. 74) of *Amber-Hi-Lites*, a quarterly publication available on ion exchange from Rohm and Haas Co., Resins Dept.—Ion Exchange, Philadelphia 5, Pennsylvania. The advantages and disadvantages of distillation and deionization are treated, and the circumstances under which one is preferred over the other are given.

● A radically designed, small glass fractional distillation apparatus has been added to the Kontes "Bantam-ware" line. The apparatus has an extremely short condensate path. Write Kontes Glass Co., 126 Spruce St., Vineland, New Jersey, for complete information.

(*Continued on page A452*)

The Welch

CATHETOMETER

Significant recent engineering improvements in this instrument insure better performance than ever and more years of satisfactory service.

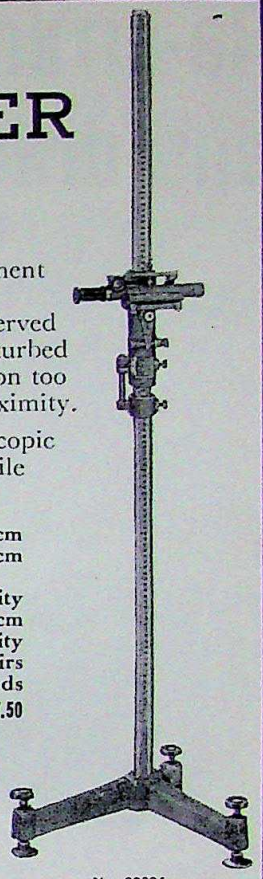
This cathetometer is designed for precise measurement of vertical distances through a range of 100 cm. It is particularly useful where the object to be observed is not conveniently accessible, or may easily be disturbed by physical contact, or must be located in a position too hazardous to permit the observer to be in close proximity.

It is also commonly employed for qualitative telescopic viewing within the laboratory because of its versatile positioning adjustments and over-all stability.

Vertical Range	100 cm
Smallest Reading by Vernier	0.05 cm
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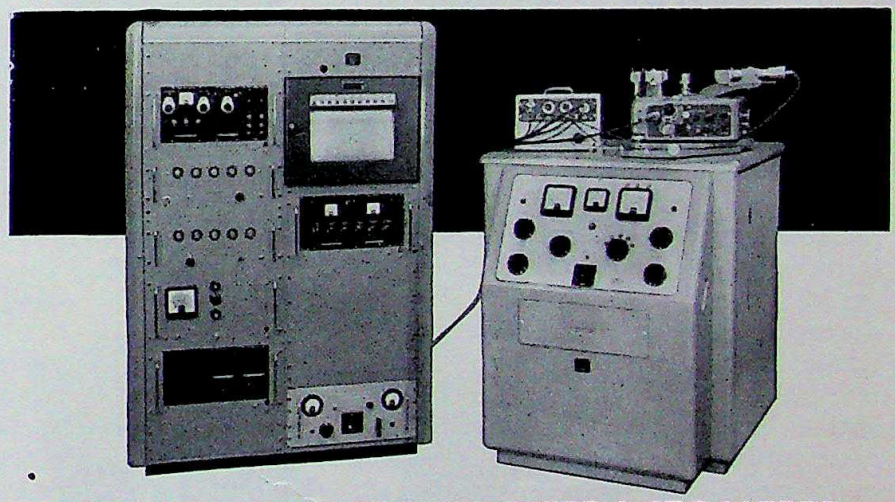
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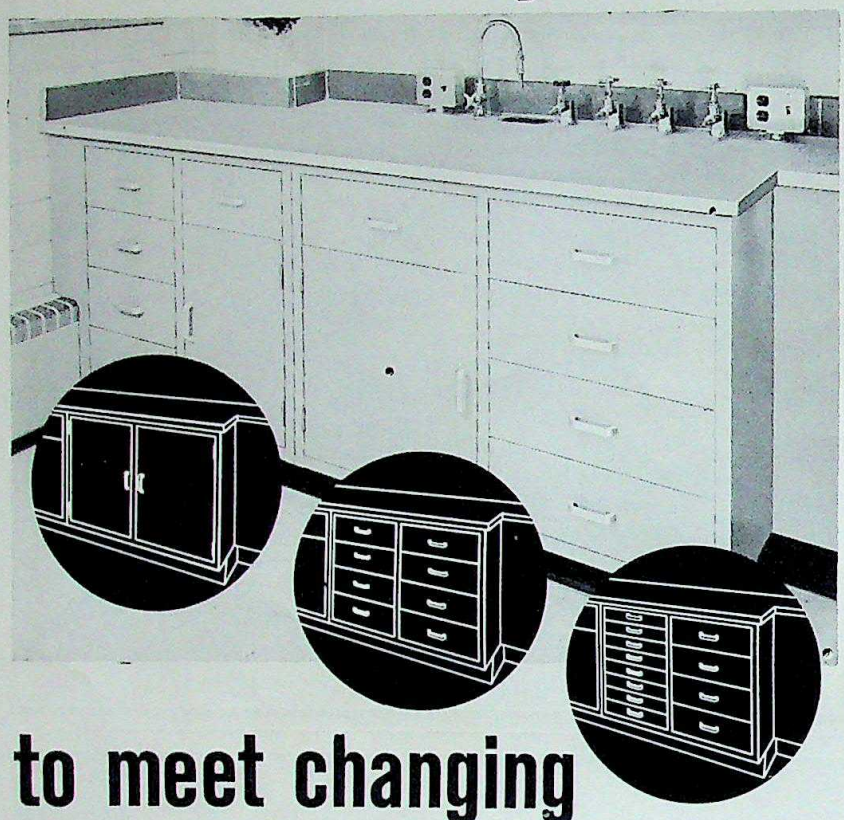
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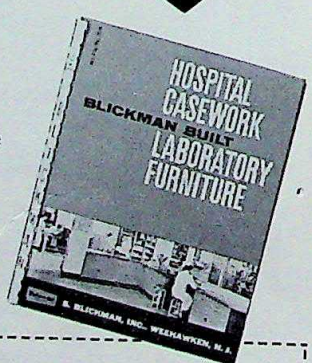
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Out of the EDITOR'S BASKET

● *Bulletin P-8* illustrates and describes in detail the five Sargent polarographs: the Models III, XII, XV, XXI, and FS. Write E. H. Sargent & Co., Dept. P-3, 4647 W. Foster Ave., Chicago 30, Illinois, for a copy.

● Copies of the newly revised *Recommended Specifications* for wood laboratory equipment may be obtained on request from: Laboratory Equipment Section, SAMA, 20 N. Wacker Dr., Chicago 6, Illinois.

● An evaluative bibliography of the scientific literature on equipment, techniques, and research results of respiratory challenge work with aerosols has been prepared and is offered to workers in the field as a service by S. Blickman, Inc., Write Tom Lanahan, S. Blickman, Inc., 536 Gregory Ave., Weehawken, New Jersey.

● Technical Bulletin 15, *Continuous Scintillation Counting of Weak Beta Emitters in Flowing Aqueous Streams*, and a six-page brochure on the new chroma/cell system for liquid chromatography with beta emitting isotopes are available on request from Nuclear-Chicago Corp., 359 E. Howard Ave., Des Plaines, Illinois.

● A brochure entitled *Safety Precautions for Storage and Processing of Volatile, Explosive or Flammable Materials* is available from Kelmore, Inc., 399 Springfield Ave., Newark 3, New Jersey. More than forty-five extremely flammable substances are listed with flash point degrees F and lower explosive limits 0/0 by volume tabulated in the four page brochure.

● A unique method for obtaining direct dew point readings without mathematical conversion is described in a new Bulletin, *No. 5991-A*, issued by Hevi-Duty Heating Equipment Co., Laboratory Equipment Dept., Watertown, Wisconsin, division of Basic Products Corp.

● A comprehensive 12-page bibliography, *Steroid Analysis by Gas Chromatography*, just released by Research Specialties Co., 200 S. Garrard Blvd., Richmond, California, covers all significant publications from 1960 through 1962. Listing is in alphabetical order by author.

● Chromatograms illustrating the major improvement in baseline stability now possible with the new Perkin-Elmer Model 800 dual column gas chromatograph are among the data in a new 12-page brochure detailing the instrument. For a copy, write: Instrument Division, The Perkin-Elmer Corp., Norwalk, Connecticut.

● To receive a copy of the *Infrared Brochure*, featuring a wide variety of infrared cells and accessories, write to Sales Dept., Isomet Corp., Palisades Park, New Jersey.

(Continued on page A454)

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FILTRATION CHART

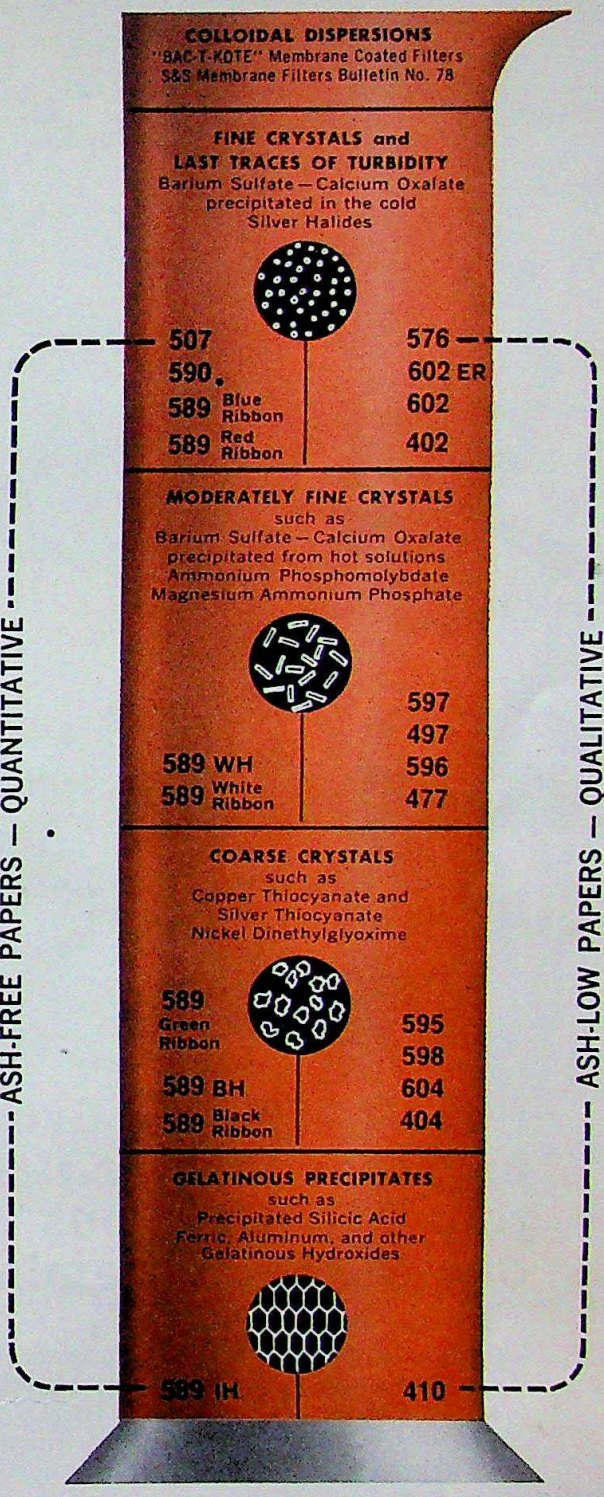
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Out of the EDITOR'S BASKET

● The Instrument Division of Varian Associates has just released an information brochure on their new laboratory magnet systems featuring "Fieldial" magnetic field regulator. Copies of this brochure are obtainable from Magnet Product Group, Varian Associates, Instrument Division, 611 Hansen Way, Palo Alto 5, California.

● Release of a 24-page Kimble catalogue and installation manual for a new line of KIMAX tempered glass drainline pipe has just been announced by Consumer and Technical Products, Owens-Illinois, Toledo 1, Ohio.

● Alpha Scientific Laboratories, P.O. Box 333, Berkeley 1, California, announce the availability of a brochure on an electron spin resonance spectrometer—*AL 340Sy.*

● Copies of Harshaw Scientific's 16-page *Laboratory Spotlight,* can be obtained by contacting Harshaw Scientific, Division of The Harshaw Chemical Co., 1945 E. 97th St., Cleveland 6, Ohio.

● Literature describing *Model 200A, Aerosol Generator* is available on request from Schoeffel Instrument Co., 355 Hillsdale Ave., Hillsdale, New Jersey.



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Miscellany

★ The second annual Thermoanalysis Institute will be held at the Madison, New Jersey, campus of Fairleigh Dickinson University. There will be a week long introductory session June 10–14 and an advanced session June 17–19. A second introductory session June 24–28 has been scheduled to accommodate additional scientists if the limited enrollment is exceeded. The program will consist of intensive lectures and laboratory sessions for which laboratory equipment will be provided by instrument manufacturers and distributors. Participants are encouraged to discuss their own areas of application with lecturers, laboratory instructors and fellow scientists. Information concerning tuition and dormitory fees for the Institute can be obtained from Dr. Saul Gordon, Director, Thermoanalysis Institute, Fairleigh Dickenson University, Madison, New Jersey.

★ During the 1963 Summer Session, Columbia University's School of Library Service again will offer a course on scientific and technical abstracting and indexing (LS S6321G). The course again will be taught by T. E. R. Singer, formerly Chemistry Librarian at the New York Public Library and now a private consultant in the field of technical information. Applications may be obtained from the School of Library Service, Columbia University, New York 27, N. Y.

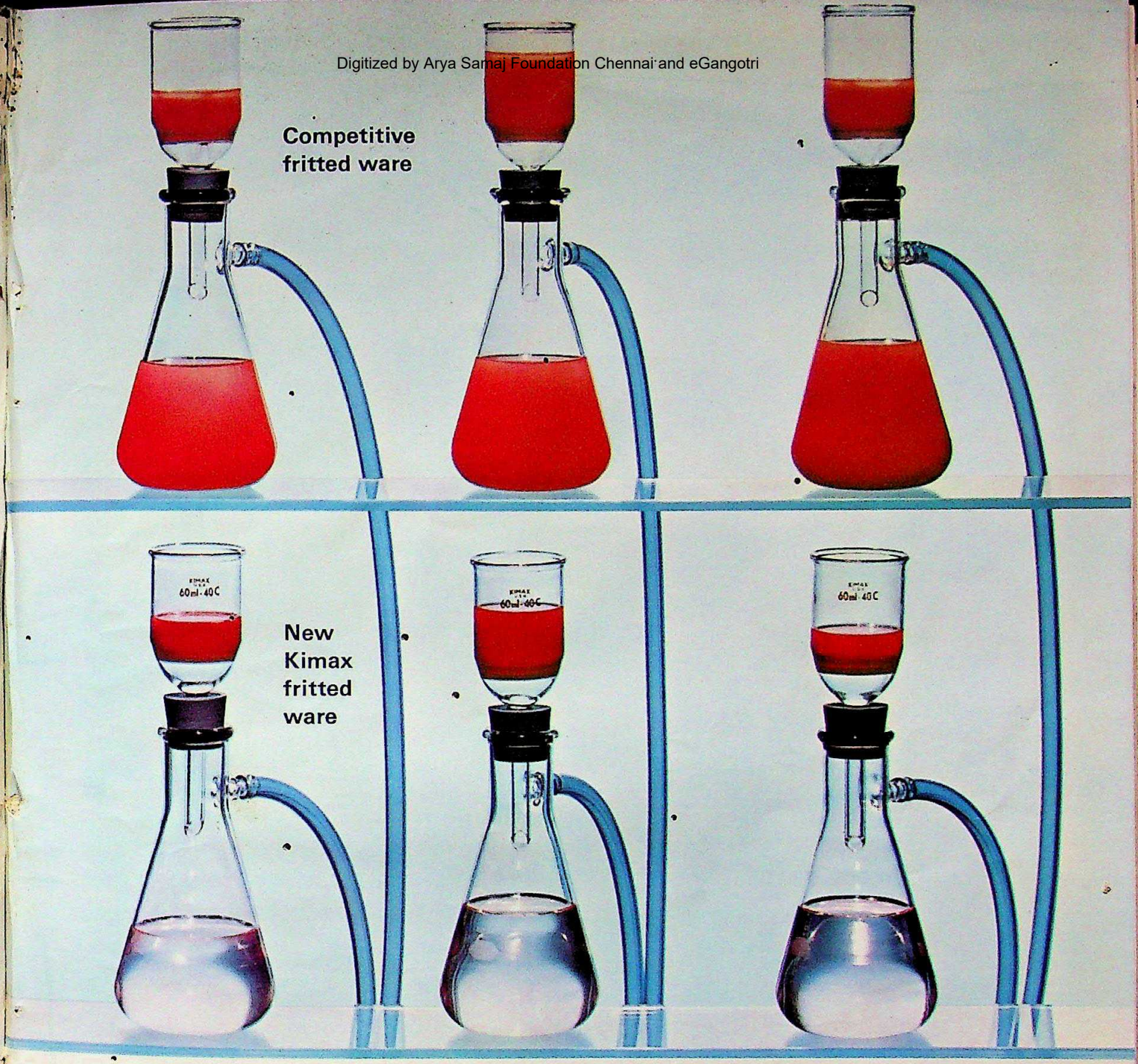
★ The department of Chemistry at Lehigh University will present the second annual Summer Symposium in Instrumental Analytical Chemistry in 1963, planned to provide the practicing analytical chemist with a background in the theory and techniques of modern instrumental analysis. Inquiries concerning program, staff, registration, costs, and other items relevant to the symposium may be directed to Professor A. J. Diefenderfer, department of chemistry, Lehigh University.

★ The 1963 Engineering Foundation Research Conferences will be held at Proctor Academy, Andover, New Hampshire, August 5–30. Four special engineering conferences are scheduled, which will focus on topics of current importance to the engineering profession. These are (1) Technology and the Civilian Economy, (2) Comminution, (3) Engineering in Medicine, and (4) Urban Transportation Research. Additional information may be obtained from Dr. Harold K. Work, Engineering Foundation, 345 East 47 Street, New York 17, N. Y.

★ Arizona State University will again offer two different and distinct courses in spectroscopy during the summer of 1963. The third annual program in Infrared and Ultraviolet Absorption Spectroscopy, August 19–30. For complete information please write to Dr. Jacob Fuchs, Director, Modern Industrial Spectroscopy, Arizona State University, Tempe, Arizona.

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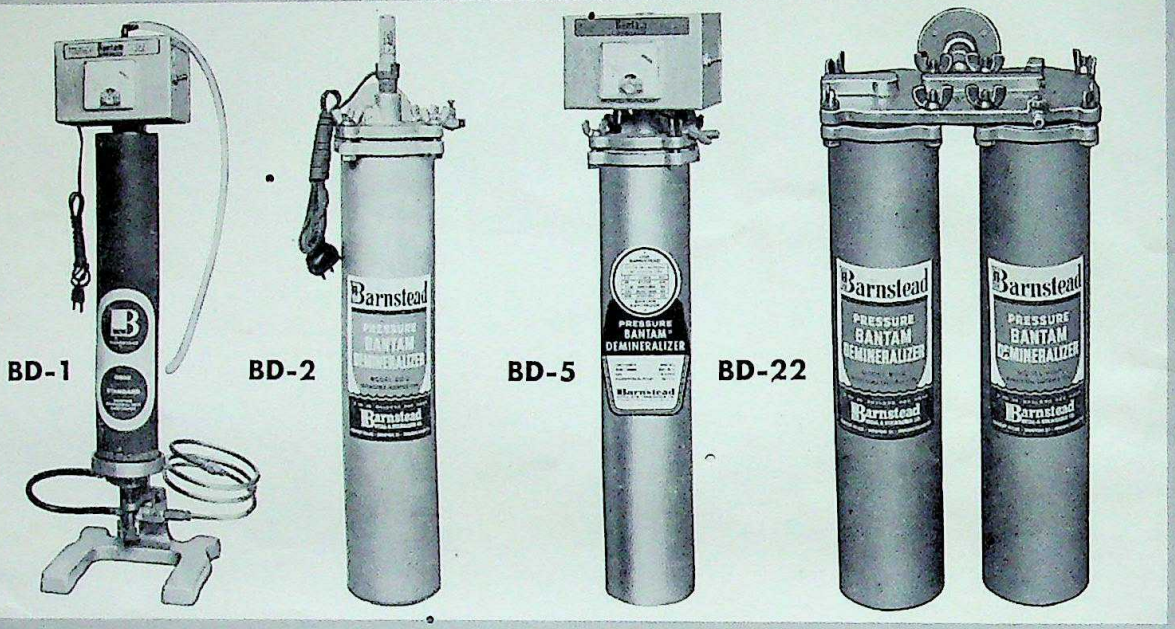
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WRITE: For Bulletin No. 154. It describes all Barnstead Demineralizers and complete line of cartridges.

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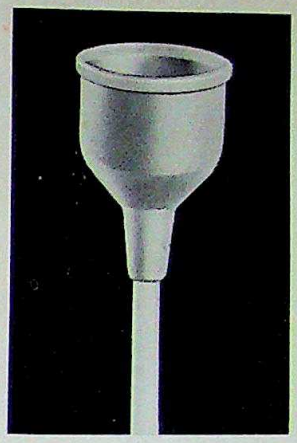
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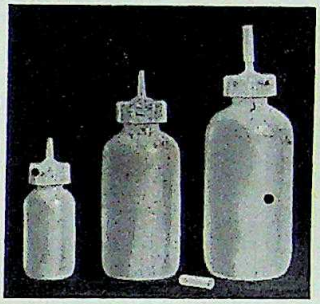
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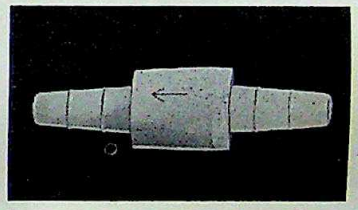
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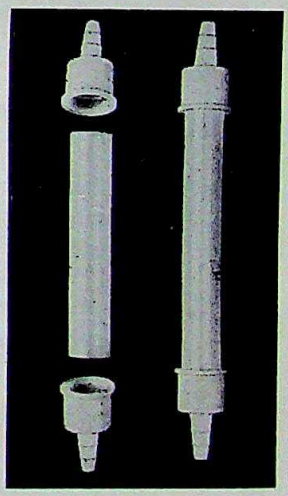


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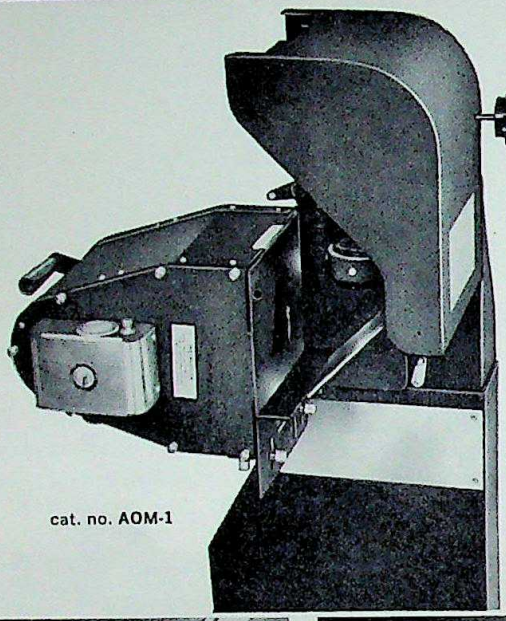
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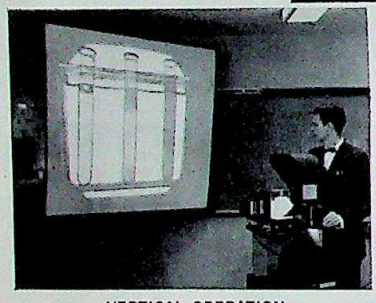
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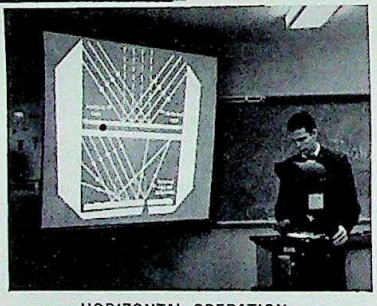
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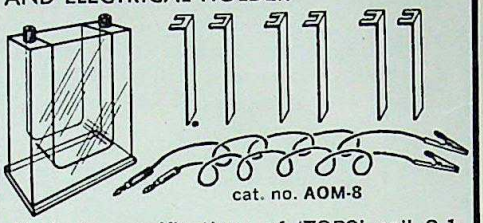
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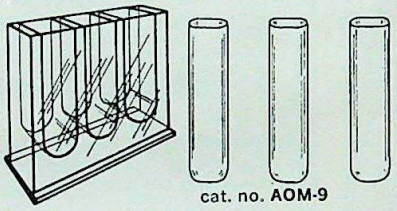
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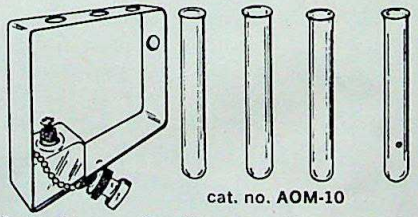
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3. HYDROGEN *(continued)*

C. Physical Properties of Hydrogen

Dem. 79—Diffusion Tube

To show: Graham's Law of Diffusion, rate of diffusion air:H_2 = $\sqrt{\text{density } H_2\text{:air}}$

Materials: Hydrogen, 2-oz square bottle, 250 ml beaker. Special device consisting of a 3-in. length of the stem of a clay pipe, stoppered at one end; and the other end cemented to a 3-in. length of glass tubing.

Procedure: Quarter-fill the bottle with water, or water colored with food coloring. Insert the glass tube in the water. Project. (*a*) Now lower an inverted beaker of hydrogen over the pipe-stem. (*b*) Remove the beaker.

Observations: (*a*) The hydrogen diffuses in four times faster than the air diffuses out of the clay stem; this increases pressure in the tube and gas bubbles out in the bottle. (*b*) When the beaker is removed, the hydrogen in the clay stem diffuses out faster than the air diffuses in; this creates a vacuum in the tube, and the liquid rises up in the tube. This is a simplified version of Dem. 77 and 78.

Dem. 80—Heat Conductivity of Hydrogen

See Special Device SD-15. A wire glowing brightly in air glows dully in helium or hydrogen; the latter conducts heat away faster.

D. Reactions of Hydrogen

Dem. 81—Rising Mothballs

To show: A novelty, for exhibit at Science Fairs.

Materials: Mothballs, dil. HCl, mossy zinc, a glass cylinder or plastic box 2 × 2 × 12 in. high.

Procedure: Fill the bottom of the plastic box 1 in. deep with mossy zinc. Fill to near the top with water. Drop in three moth balls. Now by means of a long thistle tube or funnel with plastic tubing attached to it, introduce about 20 ml. of dil. or conc. HCl. Project.

Observations: The mothballs sink to the bottom, pick up hydrogen and are bouyed to the top again, lose the gas, sink again, and so on.

Notes: *1.* This is a difficult experiment to get working, but once it does, the mothballs will rise and fall for an hour.

2. Instead of water, saltwater can be used to give the mothballs greater bouyancy.

3. Be sure the bottom of the container is completely covered with a layer of mossy or granular zinc.

4. This will not work with a bottle 5 in. high; evidently the foot of hydrostatic pressure is required to collect and release the gas bubbles easily.

Dem. 82—Dehydrogenation of Fats

To show: The dehydrogenation, cracking and subsequent bromination of bacon fat.

$$C_3H_5OH \xrightarrow{-H} H_2C{=}CH_2{-}CHO$$

$$H_2C{=}CH_2{-}CHO \xrightarrow[+Br_2]{} CH_2Br{-}CH_2Br{-}CHO$$

Materials: Strip of bacon, bromine or bromine water, forceps, alcohol burner, two 2-oz wide-mouth square bottles.

Procedure: Hold an open bottle of bromine to the mouth of each bottle, to fill them equally with bromine gas. Set the alcohol burner on the stage beside them and project. Cut a tiny slice of bacon $^1/_4$ × 2 in. and hold it in the burner flame, using the tongs; then lower the burning, dripping bacon into one of the bottles of bromine.

Observation: The bacon drippings decolorize the bromine. Reason: heating cracks glycerin in the bacon fat into acrolein, $H_2C{=}CH_2{-}CHO$. This unsaturated compound adds bromine forming $CH_2Br{-}CH_2Br{-}CHO$.

Notes: *1.* Culture tubes and C-g2(SD-7) can be used, but the bottle is more convenient.

2. If bromine is not available use bromine water, or even KBr-aq. to which a small amount of chlorine water has been added (not excess). But Br-vapor is preferable.

Dem. 83—Dehydrogenation (Oxidation) of Methanol

To show: The catalytic dehydrogenation (oxidation) of methyl alcohol.

$$\underset{\text{methyl alcohol}}{CH_3OH} - (2H) \xrightarrow[\text{catalyst}]{Cu} \underset{\text{formaldehyde}}{HCHO}$$

or

$$2CH_3OH + O_2 \xrightarrow[\text{catalyst}]{Cu} 2H_2O + 2HCHO$$

Materials (*a*). Alcohol burner, 6-in. of No. 16 bare Cu wire, 4 culture tubes, cell H-3. (*b*) *Tollens reagent.* To 20 ml of 0.1 *M* $AgNO_3$ add NH_4OH until the precipitate which first forms *just* dissolves. Use at once, do not store. (*c*) *Schiff's reagent.* Dissolve 0.1 g roseaniline hydrochloride in 100 ml of water. Filter to remove all solids. Add pinches of sodium meta bisulfite until the pink color just bleaches. Filter again, if necessary. This solution can be used at once or preferably after it has stood 24 hr.

Procedure: (*a*) *Catalytic dehydrogenation* (*oxidation*). Fill a culture tube one-third full of methyl alcohol. Place in cell H-3 and project. Wind the Cu wire into a spiral which slips easily into the culture tube, and bend the upper end so the spiral hangs suspended a quarter inch above the alcohol. Heat the spiral, and lower it red-hot into the tube. Stopper with the thumb and shake to dissolve any vapors of aldehyde

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formed. Repeat two more times. To treated and untreated samples projected in cell H-3 add an equal volume of Tollens reagent. Shake. Now heat both samples. (*c*) *Schiff test.* Cool the treated sample by pouring into another culture tube at room temperature. To this sample and an untreated sample of methyl alcohol add 10 drops of Schiff's reagent, with the tubes being projected in cell H-3 or C-g.

Observations: (*a*) As the copper wire glows, oxide and metallic colors flash over its surface. The odor of formaldehyde is observed in the treated tube. (*b*) Formaldehyde in the treated tube forms with Tollens reagent a silver mirror; on the projector this tube grows dark-brown and finally black. The untreated tube remains clear. (*c*) Formaldehyde in the treated tube forms, with Schiff's reagent, pink aldehyde-amine complex; the untreated tube remains clear.

Dem. 84—Adsorption of Hydrogen by Platinum

To show: The adsorption of hydrogen by platinum will catalyze the explosive combination of $2H_2 + O_2$.

Materials: Oxygen, hydrogen, 1-oz wide-mouth square bottle and stopper, wad of platinized asbestos, forceps.

Procedure: By displacement of water, fill the bottle $^2/_3$rds full of H_2 and $^1/_3$rd full of O_2, and stopper. Place on stage and project. Remove stopper and, holding the wad of platinized asbestos in forceps (CARE) drop the wad into the bottle of gas.

Observations: The platinum absorbs hydrogen, glows, and ignites the $2H_2 + O_2$. The resulting explosion blows the wad of catalyst out of the bottle.

E. Hydrogen Isotopes

Dem. 85—Deuterium Oxide

To show: The difference in F.P. of H_2O versus D_2O.

Materials: Sealed culture tubes half-full of water and of heavy water respectively, Cell C-g2(SD-7), salt-ice mixture.

Procedure: Place the culture tubes with the two samples in the salt-ice mixture. When both have solidified, place them simultaneously in cell C-g2, and project.

Observation: After some minutes the H_2O (m.p. 0°C) will melt, and then the D_2O (mp 3.82°C) will follow suit.

Note: The demonstration can be reversed by placing the tubes of liquid in ice-salt mixture and seeing which one freezes first (the D_2O). However, supercooling can occur delaying the action.

SUPPLEMENTARY DEVICES

SD-15—Heat Conductivity of Gases

To show: That hydrogen and helium conduct heat much more efficiently than air.

Construction of SD-15. See Figure SD-15. Current from 110 v ac line passes through a 600-watt conical heating element, thence via a 2-in. $^{10}/_{32}$ machine screw to 2-in. of No. 28 Chromel-A resistance wire, and finally to a $3^1/_2$-in. brass rod $^1/_4$-in. in diameter. The resistance wire should glow brightly without burning out. Achieve this by (*a*) using a larger or smaller wire or (*b*) cutting off some of the heating-element wire.

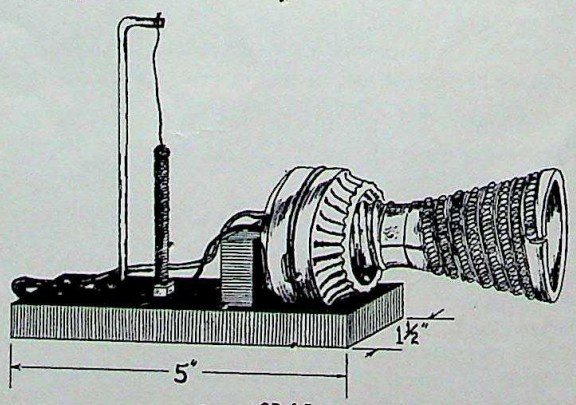
Note: Instead of using 110 v ac, and a conical heating element, the wires can lead from a 12-v dc storage battery through an on-off switch mounted on the 5 × $1^1/_2$ × $^1/_2$-in. plastic base to No. 34 Chromel-A resistence wire.

Procedure with helium: Set the device on the stage with the heating unit projecting into the room (CARE). (*a*) Plug in the device but not the projector; darken the room. (*b*) Now lower a 2-oz square bottle or a 25 × 200-mm test tubeful of helium gas over the glowing wire.

Observations with helium: (*a*) In the absence of the projector light, the light of the glowing filament can be focussed on the screen. (*b*) The wire which glows so brightly in air is hardly visible in an atmosphere of helium. Reason: heat is conducted away from the wire rapidly by the helium. This illustrates the principle of a Pirani Gauge, where the extent of a vacuum is measured by the conductivity of a wire heated in it.

Procedure with hydrogen: DANGER OF MINOR EXPLOSION. Perform in one of two ways. (*a*) Fill a 25 × 200-mm test tube with hydrogen, and stopper. Project device SD-15, and show the filament glows 10 sec after plugging in. NOW TURN OFF THE CURRENT. Lower the tube of hydrogen over the *cool* wire, then turn on the current for 10 sec. TURN OFF THE CURRENT. (*b*) Place the inverted tube over the wire and run hydrogen in continuously while turning on the current. Turn off the current, remove the tube, then turn the current on again.

Observations with hydrogen: There will be no explosion so long as the hot filament is completely surrounded by hydrogen; otherwise a startling but not dangerous pop occurs. In each case the wire glows in hydrogen but not in air.



SD-15

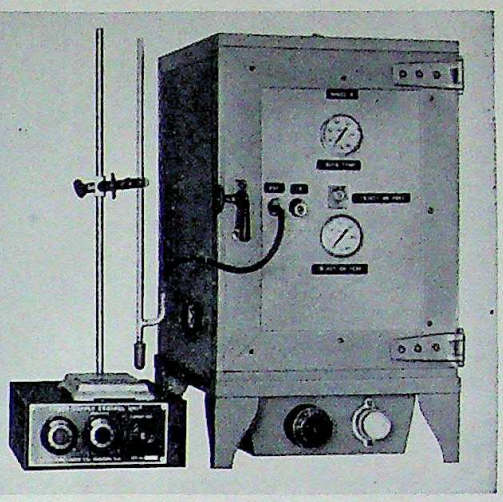
(*To be continued in July*)

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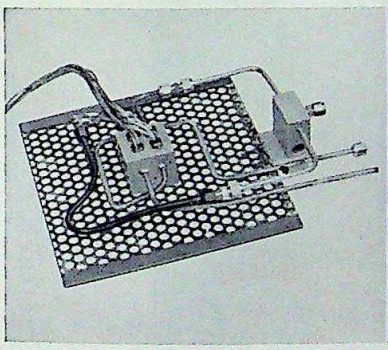
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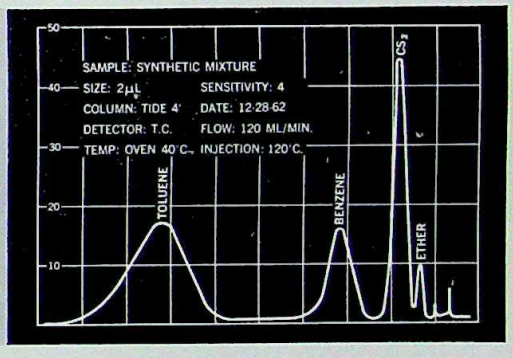
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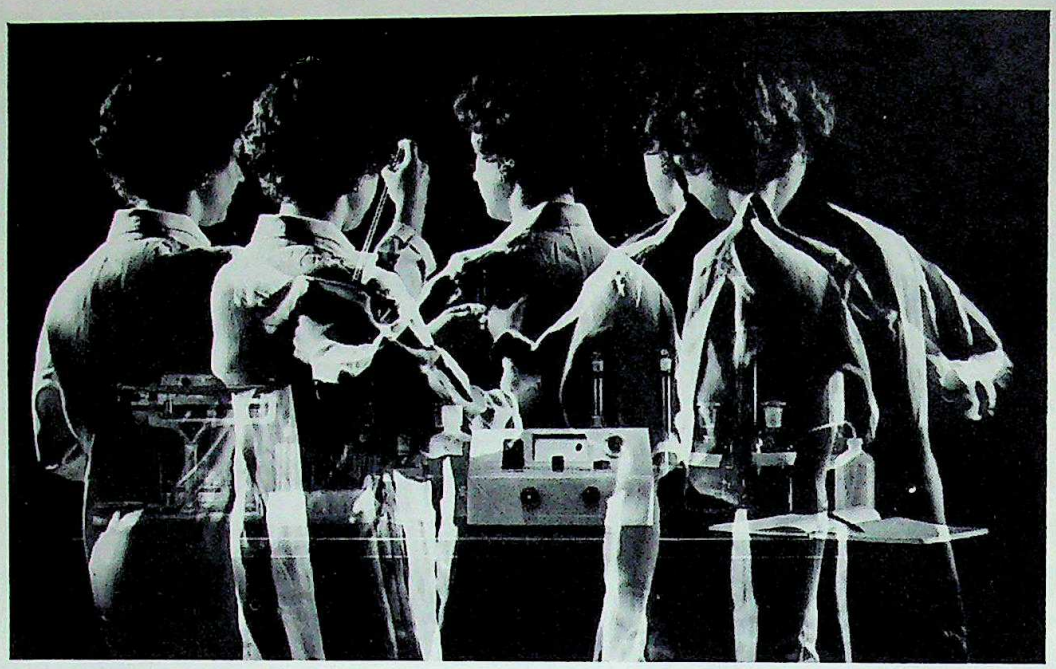
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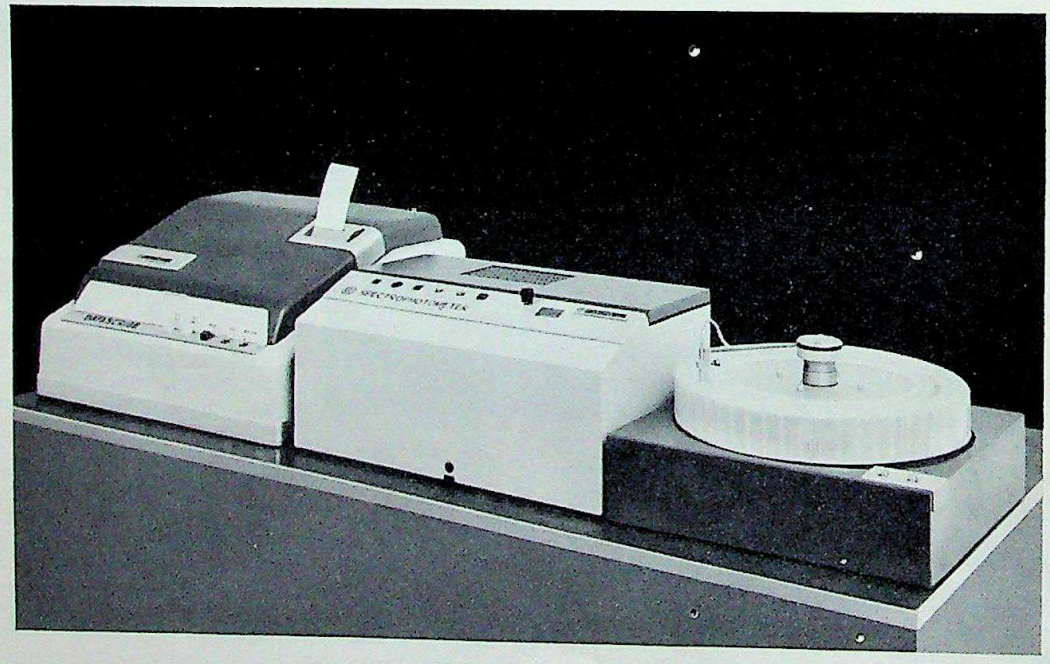
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a ChemEd feature

CHEMICAL PROJECTS

Research Ideas for Young Chemists

Compiled by **JAY A. YOUNG,** King's College, Wilkes-Barre, Penna.
JOHN K. TAYLOR, National Bureau of Standards, Washington, D. C.

Apparatus for the Friedel-Crafts Reaction

See KREMER, C. B., AND WILEN, S. H., *J. Chem. Educ.*, **38**, 306–7 (1961).

An ingenious modification of the apparatus assembly usually employed for a Friedel-Crafts reaction is described in this article. No special pieces of apparatus are required; the components can be readily assembled or dissembled. Reasonable quantities of reagent can be used.

Questions:

What other compounds can you synthesize, using the apparatus described in the article, in addition to the four hydrocarbons which are specifically mentioned?

Can you adapt the apparatus described in the article for use on a semimicro scale?

In the article it is stated that there is no need to use a reflux condenser with the apparatus and, further, refluxing would probably increase the amount of polysubstitution. Will refluxing increase the amount of polysubstitution? If so, can you account for this effect? Test your hypothesis by further laboratory work.

Select another type reaction from those often used in organic syntheses and modify the apparatus assembly usually used so that it will be more convenient to use, as Professors Kremer and Wilen have done for the Friedel-Crafts reaction.

The Pyrolytic Decomposition of Carboxylate Salts to Ketones

See SCHULTZ, H. P., AND SICHELS, J. P., *J. Chem. Educ.*, **38**, 300–1 (1961).

In some textbooks of organic chemistry it is stated that when dry calcium acetate or barium acetate is heated, acetone is formed as a major product. In fact, this statement is not warranted by the results of laboratory studies especially when, as some textbooks also state, it is concluded that pyrolytic decomposition of carboxylate salts yields carbonyl compounds as the major product. The authors cite several examples to show that many different products are formed by this kind of pyrolytic decomposition.

From the examples cited, it is evident that additional controlled studies of the pyrolytic decomposition of various carboxylate salts are needed in order to assemble the data required for an explanation of the mechanism of pyrolytic decompositions of carboxylate salts. See also THIS JOURNAL, **38**, 638 (1961).

Questions:

Select a series of carboxylate salts of homologous acids, for example, calcium acetate, calcium propionate, calcium butyrate, and so on. Determine, as quantitatively as possible, the relationships among the type of salt, the conditions of pyrolysis, and the pyrolysis products. For further work, repeat the initial studies, using some other series of salts, such as barium acetate, barium propionate, and so on, and continue similarly, using series of salts of other metals.

Or, compare, in a quantitative manner, the relationships among the type of salt, the conditions of pyrolysis, and the pyrolysis products, for the pyrolytic decomposition of calcium barium, and strontium acetate; or lithium, sodium, and potassium oxalate. Other similar groups of comparable metal salts can also be studied.

From the results which you obtain, can you predict the pyrolysis products which would be formed when another carboxylate salt is decomposed by heating? Test your prediction in the laboratory.

Polystyrene—A Multistep Synthesis

See WILEN, S. H., ET AL., J. CHEM. EDUC., **38**, 304–5 (1961).

This synthesis of polystyrene involves a series of preparative steps, each illustrating an interesting technique or reaction, or both, in the synthesis of the required intermediate compounds.

Questions:

Can you obtain a better yield of final product than that reported in the article? If so, account for the improvement and test your explanation by further laboratory work.

Synthesize polystyrene, identifying each of the intermediate compounds by studying and characterizing their chemical and physical properties.

Derivatives of polystyrene in which substituents are located on the aryl ring have been prepared. Can you prepare any such derivatives by starting, for example, with toluene, or phenol, or other benzene derivative instead of starting with benzene? Does your polymer differ from polystyrene? Account for these differences.

Is it necessary to use dibenzoyl peroxide as a catalyst for the polymerization of styrene? Will some other catalyst also work? If so, account for this fact and test your explanation by further laboratory work.

NOTE: Students who elect to study these questions should first familiarize themselves with the safety precautions to be observed for the use of sodium borohydride and dibenzoyl peroxide.

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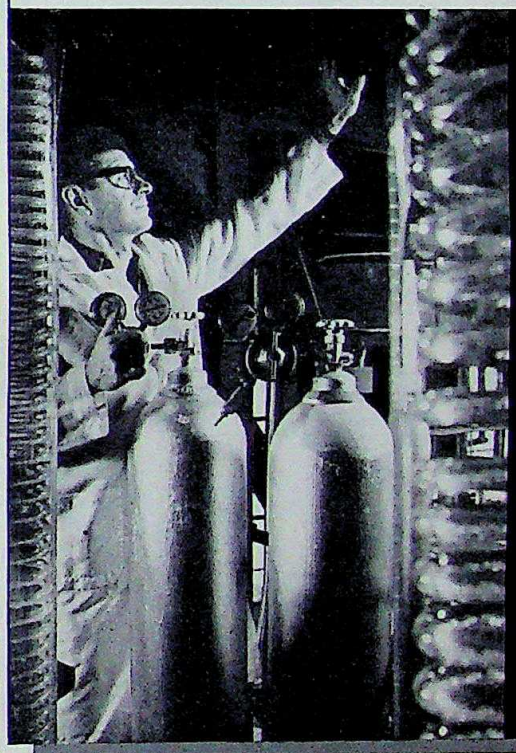
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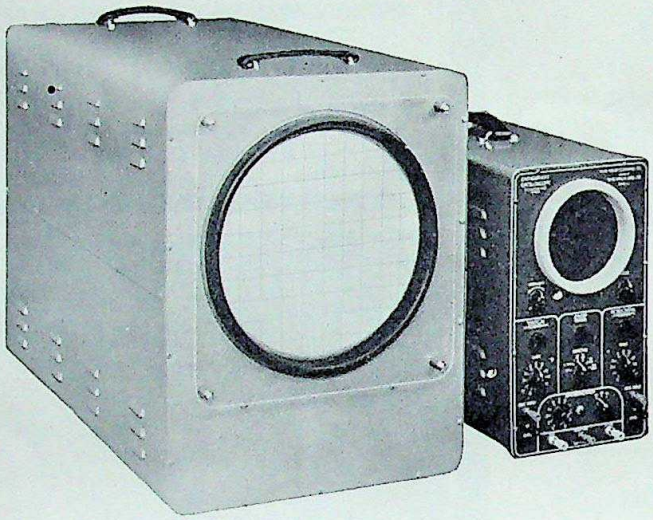
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Chem Ed

EDITORIALLY SPEAKING

The end of the academic year is an appropriate time to take a look at an ever-present problem: putting ideas into words on paper. The split-in-two life of editor and professor coalesces at this time of year. Theses and student reports on the professorial corner of the desk have many features in common with the manuscripts accumulating on the editorial corner. Both stacks contain well-written papers; both have some in which the author's ideas remain a complete mystery to the reader. Rather than dwell on the implications of oversimplified comparisons, we will be obvious about our conclusions: If more professors paid attention to how their students write, editors would stand up and cheer. Furthermore, tossing all subtlety aside, we hope that professors, once they have gotten the habit of defining and condemning sin, will practice what they preach!

Instead of giving readers another list of "Do's and Don'ts" or repeating discussions of the problem much better presented in the many good books on technical writing, we will let some eloquent examples speak for us. The following all actually have appeared in papers which presumably the authors thought were appropriate for publication. They are all from the "Ouch!" file and are presented here on what might be called a "sic!" page.

First, see what trouble Pied-Piper prepositions can lead to:

> . . . The purpose of the book is according to the authors to acquaint the future teachers with the simplest methods of the chemical analysis, to develop their ability of independent laboratory work, and as a result of the studying of the methods of determination of the composition of substances—to consolidate their knowledge of inorganic chemistry.

A forlorn little "it" sometimes cannot be sure of its obligations to the rest of the sentence. The first of the following received blue-pencil help; the second was not worth saving.

> . . . Thus accidental cracking or breaking of the flask results in the aluminum-paint-coated steel cylinder retaining the liquid until it can be disposed in a proper manner.

> . . . Although plant visits require careful preparation and much effort, the satisfaction of seeing the students learn about new and fascinating experiences makes it worth while.

Enthusiasm often fools an author into thinking that adjectives and figures of speech can substitute for facts:

> . . . It is not difficult to stay in the mainstream of chemical theory, nor is it beyond reach to present a logical scheme; the exhilarating problem has been the production of a continuous laboratory foundation for theory.

Other authors seem to be afraid that information will confuse the issue when opinions are at stake. Furthermore, if a fact does creep in, it has to be disguished by qualifying phrases to be acceptable.

> . . . There is evidence that there has been advance in acceptance and pragmatic recognition of the principle that the content of chemistry functionable in nursing and education for the profession includes basic principles of the branches inorganic, organic and physiological chemistry or biochemistry. One may infer that there is harmony or high degree of agreement with this point of view.

> . . . We have found the problem of placing a minimum knowledge of science as an essential part of the life goals of the student has been extremely simplified by the use of the intellectual framework of the social process which is based upon a relatively small list of value categories under which just about all the goals to which men aspire can be classified.

Readers can imagine how excessively long the manuscript was which began with the following. There was no ten-cent word in it if a twenty-five or fifty-cent word would do:

> The greatest inhibition in planning for the instigation of a laboratory course in practices of instrumentation, lies in the well-warranted assumption that a prohibitive investment in elaborate equipment is required.

The file is not empty, but the page is full. Enough is enough—for now!

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J. L. Franklin
Humble Oil and Refining Company
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The Chemical Behavior of Ions in Gases

This paper will discuss ions in gases. It is, I fear, a rather esoteric topic to chemists who are used to thinking of ions as existing in solution where the solvent supplies the rather large amount of energy required to bring about the formation of ions from neutral molecules. The solvent, of course, accomplishes this by vigorous interaction with the electric charge of the ion, with the result that the ion is never isolated but is always accompanied by its retinue of solvent molecules. Indeed, it was because we wished to study the behavior of pure ions, unaccompanied by solvent, that we engaged in these researches into the chemistry of ions in gases.

In order to generate a positive ion in the gas phase we must supply the necessary energy by some means other than solvation. In our studies we have employed low energy electrons to supply the necessary energy; and in order to introduce the energy into the molecules somewhat selectively and to obtain interpretable measurements for individual ionic species, we have worked at rather low pressures. In our studies we consider 10^{-5}–10^{-6} mm of mercury as low pressure and 0.01–0.5 mm of mercury as high pressure. Except at the very highest end of this pressure range we can look upon each ion or molecule as an isolated system that will have very small probability of undergoing collision during the brief time of retention in our apparatus. Consequently, whatever energy is imparted to the molecule must be imparted at a single collision with an electron; any change that occurs must result from this one impact and must occur in quite a short time (about 10^{-6} sec); energy transferred to the molecule by the electron will go to excite internal modes and will not alter the momentum of the molecule.

The most convenient and satisfactory device for accomplishing our desired objectives was a mass spectrometer and in all of our investigations one of several such instruments has been employed. Most of our work has been conducted with sector field instruments but some employed a cycloidal instrument as well. A sector field instrument is shown diagrammatically in Figure 1 together with typical operating conditions.

When a narrow beam of electrons passes through the gas in the ion source some will collide with molecules of the gas. If the energy of the electrons is sufficient, electrons in the molecule will be excited to higher orbitals or removed completely, forming an ion. In some instances more than one electron may be affected. Thus a track of positive ions is formed along the course

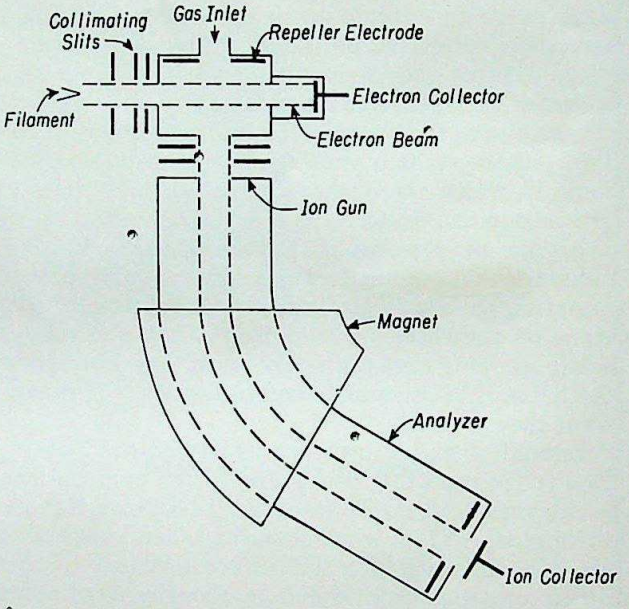
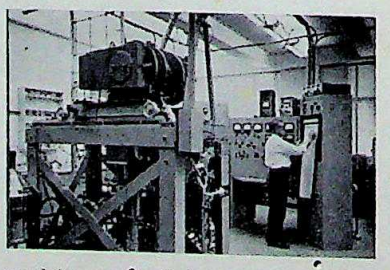


Figure 1. Schematic diagram of sector field mass spectrometer. Electron energy 8-70 v. Electron current 0.1-3μ amp. Repeller electrode voltage 5–20 v. Ion accelerating voltage 2000 V. Ion current 10^{-10}–10^{-12} amps. Source temperature 150°C. Gas pressure—ionization chambers $\sim 10^{-6}$ –1.0 mm Hg, analyzer tube $\sim 10^{-7}$–10^{-5} mm Hg. Magnetic field 300–3000 gauss. Ionization chamber dimensions: length, 7 mm source A; 20 mm source B; depth, 4 mm; distance, center of electron beam to ion exit slit, 2 mm.

The Cover



The photograph shows Mr. Wilburn C. Gieger operating the mass spectrometer used for much of the work here discussed. The heavy installation on the tracks is the magnet. The upper part of the analyzer tube and ion collector are in the top center of the picture. The lower end of the analyzer tube emerges from between the magnets in the center. The ion source and gas inlet tube can be seen extending diagonally downward in the lower center behind Mr. Geiger.

This address was given by Dr. Franklin on the occasion of the presentation of the Southwest Award to him at the Southwest Regional Meeting of the ACS in Dallas on December 7, 1962. The author had this to say by way of introduction. "The only duty required of the winner of the Southwest Award is to present an address to the Southwest Regional Meeting of the American Chemical Society upon some aspect of his research. Our laboratory has been engaged principally in studies of the chemistry of ions in gases at low pressures and it therefore seems in keeping with the spirit of this occasion that I present a brief survey of our studies of these phenomena. Before doing so, however, I must acknowledge my indebtedness and my profound gratitude to my colleagues in research and especially to Drs. Field, Lampe, and Munson, and Mr. Geiger, whose collaboration has gone far toward making this occasion possible."

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of the electron beam and these are impelled toward the exit slit by a small electric potential applied at the repeller electrode. The ions pass out into the ion gun where they are accelerated by an electric field to a controlled energy and passed into a magnetic field where their paths are caused to curve, the greater the e/m (charge to mass ratio) the greater being the curvature. By properly adjusting the accelerating potential and the magnetic field, ions of a given e/m can be focused upon the collector where their abundance may be measured as an electric current.

If the analyzer is focused upon a certain ion and the energy of the electron beam is gradually reduced, the intensity of the ion beam will diminish correspondingly along a curve similar to those shown in Figure 2. If the reduction of electron energy is carried far enough, the ion current will diminish to zero. The electron energy at which this occurs is the appearance potential. The curvature at the foot of the curve is attributable in part to the thermal spread in energy of the electrons and in part to any low-lying excited states of the ion. If the curve in Figure 2 is extended upward sufficiently, it will eventually reach a broad maximum and then gradually decline as the electron energy increases. We will not be concerned, however, with the upper portion of the ionization efficiency curve.

An electron traveling with sufficient energy to ionize a molecule will be "in contact" with the molecule for a period in the order of 10^{-14} to 10^{-15} sec. Since even rather rapid vibrations require time greater than 10^{-13} sec, it is evident that the time for ionization is much less than the time of a vibration. As a consequence, the configuration of the ion immediately after its formation will be essentially the same as that of the molecule at the time of impact. Any decomposition or adjustment of the ion into a more favorable configuration will necessarily occur later. This is the well-known Franck-Condon principle[1] and, expressed simply, requires that ionization by electron impact involve a vertical transition from molecule to ion. Figure 3 *a–c* give an example of the behavior of several simple systems according to the Franck-Condon principle. For the system in Figure 3*a*, the ground state of AB^+ falls within the Franck-Condon region and one would expect the appearance potential of AB^+ to correspond to the ionization potential of AB. On the other hand, the repulsive portion of the attractive curve does not intersect the Franck-Condon region opposite to the decomposition asymptote and so the A^+ ion will not be formed in the ground state. It will, however, be formed from the repulsive curve with excess energy. Figure 3*b* shows a system in which the Franck-Condon region does include the decomposition asymptote. Careful measurement of the appearance potential of A^+ should yield the energy required to form A^+ and B in their ground states. Figure 3*c* shows a system in which the Franck-Condon region intersects the potential energy curve of AB^+ above the decomposition asymptote. Here AB^+ would not be observable and the decomposition products would be formed with excess energy. We can, of course, treat the appearance potential as a heat of reaction so that for the reaction

$$AB \rightarrow A^+ + B \qquad (1)$$

[1] For a more complete discussion, see FIELD, F. H., AND FRANKLIN, J. L., "Electron Impact Phenomena," Academic Press, New York, 1957, p. 157.

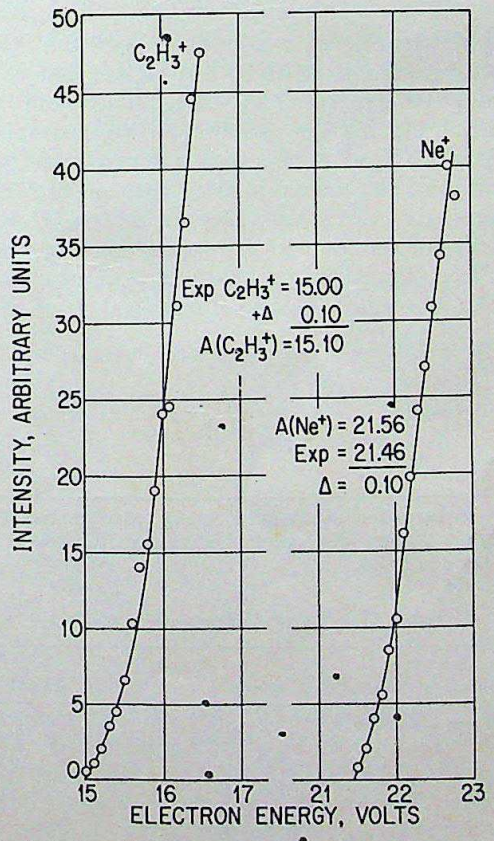


Figure 2. Ionization efficiency curves.

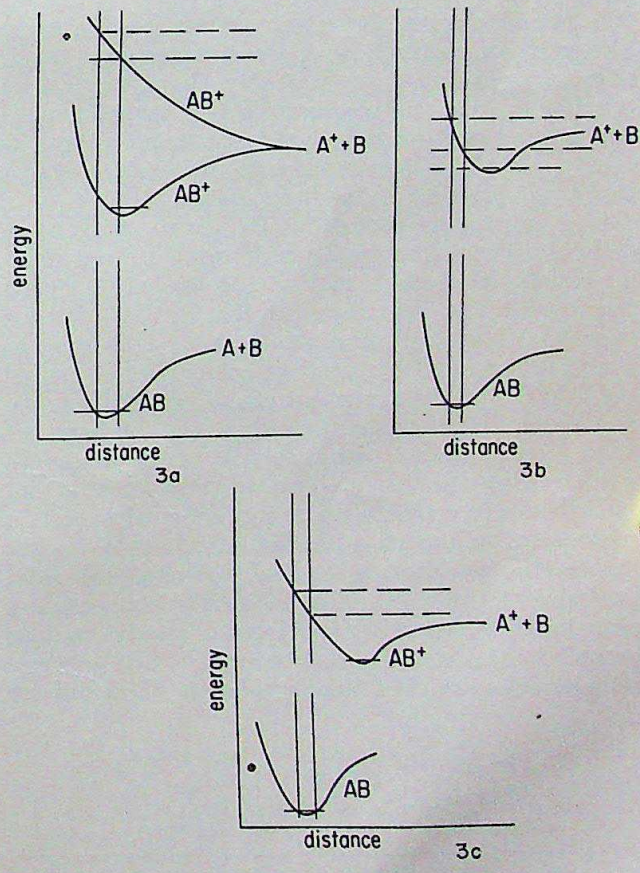


Figure 3.

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we may write

$$Ap = \Delta H_f(A^+) + \Delta H_f(B) - \Delta H_f(AB) + E_{ex} \quad (2)$$

where E_{ex} is excess energy. An equivalent statement is

$$Ap = D(A - B) + I(A) + E_{ex} \quad (3)$$

where D and I are bond strength and ionization potential, respectively.

From these considerations one would suppose that the appearance potential of most parent ions would be greater than the adiabatic ionization potential, and indeed this is usually the case although with most molecules the difference is small (<0.1 ev). One would also predict that most fragment ions would be formed with excess energy but, surprisingly, this is usually not the case. Although the appearance potential of a given ion from a single compound will always be suspect, one would place considerable confidence in the value if essentially the same heat of formation of the ion is obtained by measurement of its appearance potential from several compounds. Table 1 gives values of $\Delta H_f(CH_3^+)$ from a variety of compounds.[2] All but two

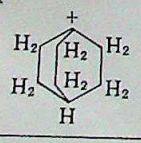
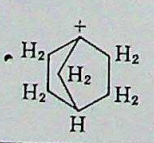
Table 1. Heat of Formation of CH_3^+ (kcal/mole)

	ΔH_f (kcal/mole)	Measured excess energy correction applied
$CH_3 \rightarrow CH_3^+ + e$	259–265	
$CH_4 \rightarrow CH_3^+ + H + e$	260–264	
$C_2H_6 \rightarrow CH_3^+ + CH_3 + e$	270	16[a]
$C_3H_8 \rightarrow CH_3^+ + C_2H_5 + e$	268	46[a]
$CH_3Cl \rightarrow CH_3^+ + Cl + e$	263	
$CH_3Br \rightarrow CH_3^+ + Br + e$	261–269	
$CH_3OH \rightarrow CH_3^+ + OH + e$	263	

[a] Ref. (*14*).

were calculated directly from the appearance potential; two were corrected for excess translational energy. The precision, although far poorer than is routinely obtained by calorimetry, is probably about as good as could be expected for measurements by several experimenters employing a variety of instruments. We conclude that $\Delta H_f(CH_3^+)$ is close to 262 kcal/mole and that this represents the ion in its ground state.

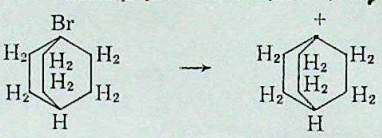
It is noteworthy that $\Delta H_f(CH_3^+)$ is the same when determined from fragmentation processes as from direct ionization of methyl radical. Molecular quantum theory predicts a planar configuration for CH_3^+ and one expects CH_3 radical to be planar also. This expectation was borne out by spectroscopic studies of methyl radical (*1*) and the agreement of $\Delta H_f(CH_3^+)$ from the two sources implies that the radical and ion have the same configuration, presumably a planar one. To further elucidate this problem we undertook in our laboratories to compare the energy required to form a planar carbonium ion with that required to form a carbonium ion that is sterically constrained from achieving planarity (*2*). Table 2 shows the appearance potential of three tertiary ions formed from the tertiary bromide. The *t*-butyl ion is free to achieve its preferred configuration, which should be planar. The ions are


and


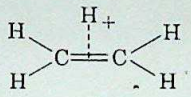
[2] Unless otherwise stated, energy values were taken from Field and Franklin, see footnote 1.

constrained with increasing rigidity from becoming planar. Table 2 shows that the appearance potential increases as the bonds to the charged carbon atom are increasingly restrained from becoming planar. Indeed the difference in appearance potential between the *tert*-butyl and 2,2,1-bicycloheptyl ions is about what would be expected for the difference between a planar and a tetrahedral (i.e., an sp^2 and an sp^3) ion. These observations lend further support to the idea that carbonium ions are planar in preferred configuration.

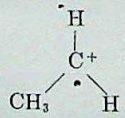
Table 2. Appearance Potentials of Strained Carbonium Ions (*2*)

	Ap(ev)
tert-$C_4H_9Br \rightarrow$ *tert*-$C_4H_9^+ + Br$	9.6
	9.98
	10.66

In attempting to explain the behavior of carbonium ions larger than methyl it has been argued with considerable conviction that the structure is probably that of a so-called Π complex[3], thus



However, there is no reason to believe that the ethyl radical has such a structure but rather that it has the conventional structure $CH_3—CH_2$, where the bonds to the carbon having the unpaired electron are planar, as in methyl. Now, appearance potentials of $C_2H_5^+$ by ionization of the radical and by various fragmentation processes give the same value for $\Delta H_f(C_2H_5^+)$ within the limits of accuracy of the measurements (see Table 3). Since the radical probably has a planar configuration the ion obtained from the radical must have one:



[3] For a discussion of complex theory, see DEWAR, M. J. S., "Electronic Theory of Organic Chemistry," Oxford University Press, London, 1949.

Table 3. Heat of Formation of $C_2H_5^+$

	ΔH_f (kcal/mole)
$C_2H_5 \rightarrow C_2H_5^+ + e$	226
$C_2H_6 \rightarrow C_2H_5^+ + H + e$	223
$C_2H_5ONO \rightarrow C_2H_5^+ + NO_2 + e$	229
$C_3H_8 \rightarrow C_2H_5^+ + CH_3 + e$	224
n-$C_4H_{10} \rightarrow C_2H_5^+ + C_2H_5 + e$	224
Average value for fragmentation processes	225

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Further since all ΔH_f were the same, either all of the ions had the planar structure or else the Π complex has the same heat of formation as the planar ion. If the latter is true then both may be present but there is certainly no reason to consider that the Π complex structure would predominate. Thus, it seems highly improbable that the Π complex can be the principal structure of the ethyl carbonium ion and, indeed, the existence of the complex as a structural entity seems quite improbable.

Although their separate existence in solution is difficult to establish, for many years alkyl carbonium ions have been postulated to play an important part in organic solution chemistry where the evidence points to increasing stability and ease of formation in the sequence methyl, ethyl, *sec*-propyl, *tert*-butyl. Ionization potentials and heats of formation amply support this view as will be seen from Table 4.

Table 4. Alkyl Carbonium Ions

R^+	Ip(R)ev (*15*)	$\Delta H_f(R^+)$kcal/mole
CH_3^+	9.95	261
$C_2H_5^+$	8.78	225
n-$C_3H_7^+$	8.68	218
sec-$C_3H_7^+$	7.90	194
tert-$C_4H_9^+$	7.42	175

It has long been known also that strong acids catalyze the isomerization of paraffins and it is generally postulated that the reaction proceeds through the medium of carbonium ions. Similar rearrangements of primary to secondary propyl ions are observed in Table 5. Here $\Delta H_f(C_3H_7^+)$ from several sources including *n*-propyl and *sec*-propyl radicals are given. It is evident that the ion prefers the secondary configuration and that the parent ion in almost all of the fragmentation reactions must undergo rearrangement to yield secondary ions in the process of decomposition. Further, little or no activation could be involved in the decomposition since this would show up as excess energy and result in a high value for $\Delta H_f(C_3H_7^+)$. Similar examples can be shown for the butyl ion.

Table 5. Heat of Formation of Propyl Ion

Reactant	$\Delta H_f(C_3H_7^+)$, (kcal/mole)
n-C_3H_7	218 (*15*)
sec-C_3H_7	194 (*15*)
C_3H_8	194
n-C_4H_{10}	190
i-C_4H_{10}	190
n-C_5H_{12}	191
i-C_5H_{12}	188
n-C_3H_7Cl	197
sec-C_3H_7Cl	195
n-C_3H_7ONO	218
sec-C_3H_7ONO	195

The small energy of activation noted for the decomposition-rearrangement reactions leading to the formation of *sec*-propyl is not unique; activation energies appear to be small or nonexistent for a large number of decomposition reactions, even for some that involve quite complex rearrangements. Direct ionization will usually form an ion in its ground state. If the heat of formation of the ion obtained by a fragmentation process is greater than that by direct ionization, then the excess heat of formation may be the activation energy for the decomposition reaction. Certainly the activation energy can be no greater than this excess energy. In Table 6 we compare the heat of formation of several ions by fragmentation and direct ionization processes and show the possible maximum energy of activation. These are all four-center or more complex processes and it is evident that the activation energy is quite small, in many cases probably zero. In no instance is it comparable in magnitude to the activation energy one might expect for a similar reaction of neutral molecules. It will be obvious that the activation energy here is taken as the barrier to reaction in the exothermic direction. Any endothermicity, of course, will show up as an activation energy, also, but here we distinguish between them.

Table 6. Activation Energies for 4-Center Reactions (kcal/mole)

	ΔH_R Obs	ΔH_R Min	$\Delta H^\ddagger$ max
$C_2H_6^+ \rightarrow C_2H_4^+ + H_2$	11	7	4
$C_2H_6 \rightarrow C_2H_2^+ + 2H_2$	77	68	9
n-$C_4H_{10}^+ \rightarrow C_2H_4^+ + C_2H_6$	17	17	0
i-$C_4H_{10}^+ \rightarrow C_3H_6^+ + CH_4$	7	4	3
$C_2H_4^+ \rightarrow C_2H_2^+ + H_2$	68	61	7
cyclo $C_6H_{10}^+ \rightarrow C_4H_6^+ + C_2H_4$	45	40	5
$C_2H_5OH^+ \rightarrow C_2H_4^+ + H_2O$	24	9	15
$HCOOH^+ \rightarrow CO^+ + H_2O$	75	66	9

This absence, or near absence, of activation energy for reactions of gaseous ions naturally leads one to suspect that solution reactions involving ions may also be free of activation energy. With this in mind we undertook to calculate the rate constant for several S_N1 solvolysis reactions on the assumption that the reaction rate is limited by the ionization step and that the only activation energy will be the endothermicity of this step. The heats of formation of the ions in the gas phase are all known, but to be useful with solution reactions it is necessary to obtain a value for the heat of solvation. Only rather indirect methods based upon modifications of the Born equation are available, and we employed the method developed by Latimer, Pitzer, and Slansky (*3*). This rests ultimately upon the establishment of a set of consistent ionic radii. The details may be obtained elsewhere (*4*). In Table 7, the results are given for typical calculations of the rate of solvolysis of several alkyl halides. To indicate the validity of the method the heat of the reaction

$$NH_4Cl_c \rightarrow NH_{4aq}^+ + Cl_{aq}^- \qquad (4)$$

is also given. The calculated values in all cases agree quite well with the experimental ones; indeed, the agreement is probably better than the method justifies. However, it certainly suggests that the method is

Table 7. Activation Energy of Solvolysis (kcal/mole)

	ΔH_R (calc)	$\Delta H^\ddagger$ (meas)
tert-$C_4H_9Cl \rightarrow$ *tert*-$C_4H_9^+ + Cl^-$	23	23.1
sec-$C_3H_7I \rightarrow$ *sec*-$C_3H_7 + I^-$	25	24.3
$CH_3Cl \rightarrow CH_3^+ + Cl^-$	73	...
$NH_4Cl_c \rightarrow NH_{4aq}^+ + Cl_{aq}^-$	2.0	3.6[a]

[a] Experimental heat of reaction.

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reasonably valid and that our observation of activation energy barriers (other than endothermicity) in the gas phase applies as well to ionic reactions in solution.

Ion-Molecule Reactions

Thus far this discussion has dealt with information obtained at quite low pressures in the ion source. At these conditions the probability that an ion will undergo collision in the source is negligibly small. As pressure is increased, the probability of collision increases and, at pressures in the order of 500 microns, will approximate unity. Table 8 gives the approximate mean free path of a typical small ion in our source at various pressures. Collision, of course, does not necessarily result in reaction, but in many instances reaction of the ion and

Table 8. Approximate Mean Free Path of Ions at Ionization Chamber Conditions

Pressure (mm Hg)	Mean free path, λ (in mm)	d/λ[a]
10^{-6}	70,000	2.9×10^{-5}
10^{-3}	70	2.9×10^{-2}
10^{-2}	7	0.29
10^{-1}	0.7	2.9
0.5	0.14	14

[a] d, the distance from the center of the electron beam to the ion exit slit is 2 mm d/λ is approximately the number of collisions an ion will undergo in traversing the ionization chamber.

neutral molecules does occur, and in Figure 4 we see the changes in abundance brought about in two of the principle ions from methane as pressure increases. Obviously, CH_4^+ and CH_3^+ decrease monotonically and become quite small at pressures in the order of 200 microns. Concomitantly, two ions outside the mass range of methane appear and, at the higher pressures dominate the spectrum. These are $C_2H_5^+$ (mass 29) and CH_5^+ (mass 17). Obviously these secondary ions must have been formed from the principle primary ions in the mass spectrum, since the minor ions would not have been present in sufficient number to account for these large secondary peaks. The CH_5^+ ion was first announced by Tal'roze and Lyubimova (*5*) in Russia and created considerable excitement. It has since been studied quite extensively in other laboratories, including our own, and its existence is well established.

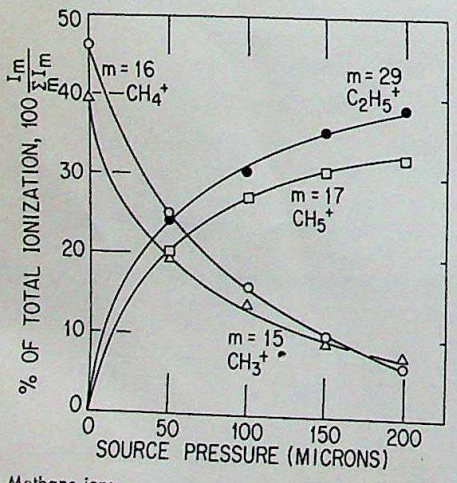


Figure 4. Methane ions.

When reactions are obviously occurring a chemist would naturally like to know the nature of the reactions. If we have a process

$$A^+ + B \rightarrow C^+ + D \qquad (5)$$

it is obvious that C^+ should have the same appearance potential as A^+. Consequently, we have depended largely upon comparing appearance potentials of secondary ions with those of primary ions in the mass spectrum in order to adduce the chemical reactions leading to the formation of the secondary ion. Thus, in Table 9 we listed the appearance potential of several primary and secondary ions from CD_4. It will be evident from these that CD_4^+ is the precursor of CD_5^+ and CD_3^+ is the precursor of $C_2D_5^+$. From this information then we write the following equations to represent the reactions in question:

$$CD_4^+ + CD_4 \rightarrow CD_5^+ + CD_3 \qquad (6)$$

$$CD_3^+ + CD_4 \rightarrow C_2D_5^+ + D_2 \qquad (7)$$

Table 9. Appearance Potentials of Primary and Secondary Ions from CD_4

Ion	Ap(ev)
CD^+	23.0
CD_2^+	15.5
CD_3^+	14.4
CD_4^+	13.1
CD_5^+	13.1
$C_2D_5^+$	14.3

In attempting to establish these reactions we must consider the question of whether in the formation of $C_2D_5^+$ two D atoms rather than D_2 might have been formed. As equation (7) is written the reaction is exothermic by about 19 kcal/mole. If, on the other hand, two D atoms were formed as neutral products the reaction would be endothermic by about 85 kcal/mole. As we will see later, these reactions proceed at very high rates; and with the very small retention time and low pressures employed, it would be impossible for us to observe reactions that involved any substantial activation energies. In fact, it can be shown that an activation energy greater than 3 or 4 kcal/mole would render the reaction too slow to be observable in our apparatus. We assume therefore that equation (7) is correct as written and that it would be impossible for us to observe had the neutral product been two atoms instead of the molecule of deuterium. We have examined quite a number of these ion-molecule reactions and, where data are available to compute the heat of reaction, we have always found the reaction to be exothermic. In fact, we now consider it to be an important criterion in determining the identity of an ion-molecule reaction that it must not be endothermic.

Now, if we admit that only exothermic reactions are observable, we can compute upper limits of heats of formation of products such as CD_5^+ where no heat of formation of the ion is available or determinable by direct means. We find, for example, that the heat of formation of CD_5^+ can be no greater than 235 kcal/mole.

Studies of ion-molecule reactions have been going forward in a number of laboratories for the past six or

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seven years, and by now an impressive body of information concerning them has been accumulated. Several reviews of research in this field are available (*6*). In spite of the fact that there has been a recent upsurge of interest in these reactions, secondary processes have been known for many years to occur in mass spectrometers. Indeed in the early days of mass spectrometry, when vacuum systems were quite primitive, they were all too prevalent and mass spectrometrists generally considered them a great nuisance. As soon as adequate vacuum systems became available mass spectrometrists went to sufficiently low pressures to circumvent secondary processes and for many years they were ignored completely. With the background of energetics and other information obtainable at the low pressures we now find that we are able to study the secondary processes effectively and profitably.

In Table 10 we list a number of kinds of ion-molecule reactions. Some of the ions that are important in solution chemistry, such as H_3O^+ and NH_4^+ are formed in the gas phase by such reactions. In addition some rather interesting new products such as H_3^+, H_2Cl^+, H_3S^+, $C_2H_6I_2^+$, etc. are observed. Table 10 includes several reactions in which a hydrogen or deterium atom is transferred, several in which a proton is transferred, and several in which a hydride ion is transferred. The latter is interesting in that it has been postulated as the chain-carrying step in alkylation and other solution reactions. It was directly observed by Field and Lampe (*7*) in our laboratories who found that the pentyl ion $C_5H_{11}^+$, which is virtually absent from the primary spectrum of neopentane, grows to considerable size as the pressure is increased. Field and Lampe showed that the reaction was as follows:

$$C_3H_5^+ + \textit{neo}\text{-}C_5H_{12} \rightarrow C_5H_{11}^+ + C_3H_6 \qquad (8)$$

The only way that this reaction could be exothermic would be if rearrangement took place in the $C_8H_{17}^+$ complex so that upon decomposition the *tert*-pentyl ion emerged. This is, of course, the gas phase counterpart of the process observed several years ago by Bartlett, Condon, and Schneider (*8*) which served as an important clue to the nature of carbonium ion chemistry

Table 10. Typical Ion-Molecule Reactions[a]

$H_2^+ + H_2 \rightarrow H_3^+ + H$
$CH_4^+ + CH_4 \rightarrow CH_5^+ + CH_3$
$H_2O^+ + H_2O \rightarrow H_3O^+ + OH$
$H_2S^+ + H_2S \rightarrow H_3S^+ + SH$
$NH_3^+ + NH_3 \rightarrow NH_4^+ + NH_2$
$Ar^+ + CH_4 \rightarrow ArH^+ + CH_3$[b]
$CH_4^+ + C_3H_6 \rightarrow CH_5^+ + C_3H_5$
$C_2H_3^+ + C_2H_4 \rightarrow C_2H_5^+ + C_2H_2$
$D_2^+ + O_2 \rightarrow DO_2^+ + D$
$I_2^+ + I_2 \rightarrow I_3^+ + I$
$HI^+ + C_2H_5I \rightarrow C_2H_5I_2^+ + H$
$CH_3^+ + C_2H_6 \rightarrow C_2H_5^+ + CH_4$
$C_2H_5^+ + C_3H_8 \rightarrow C_3H_7^+ + C_2H_6$
$C_3H_5^+ + \text{neo}C_5H_{12} \rightarrow \text{t-}C_5H_{11}^+ + C_3H_6$
$Xe^+ + CH_4 \rightarrow XeCH_3^+ + H$[c] (*12*)
$C_2H_4^+ + C_2H_4 \rightarrow C_3H_5^+ + CH_3$
$\searrow\ C_4H_7^+ + H$
$C_2H_2^+ + C_2H_4 \rightarrow C_3H_3^+ + CH_3$
$\searrow\ C_4H_5^+ + H$
$C_4H_6^+ + C_4H_6 \rightarrow C_6H_6^+ + C_2H_6$
$CH_3I^+ + CH_3I \rightarrow C_2H_6I^+ + I$

[a] Taken from reference (*6a*) unless otherwise noted.
[b] Ref. (*16*).
[c] Ref. (*17*).

It is interesting that these hydride ion transfer reactions occur very extensively in the paraffins; as will be observed in Figure 5 where we see the $C_3H_7^+$ ion increasing from a very small intensity in the primary spectrum to about 60% of all the ions present when the pressure is increased to about 150 microns. The only way that this can be accounted for is that most of the ions in the primary spectrum must have abstracted an H^- from propane leaving the $C_3H_7^+$ ion. Reactions of this kind are so common in paraffins above ethane that radiation chemists now consider that they dominate the mechanism of chemical change brought about by radiation in the paraffins.

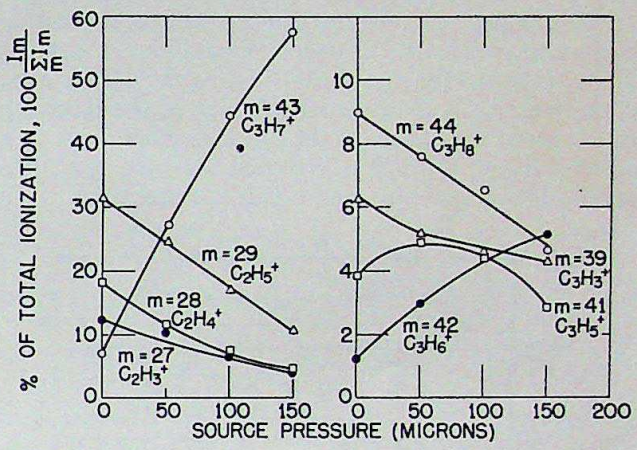


Figure 5. Propane ions.

Ion-molecule reactions are not limited to the exchange of hydrogens, however, and in Table 10 we see several reactions involving quite profound changes in the carbon structure. It is also evident that some reactants can produce several sets of products by different reactions.

Ion-molecule reactions are not necessarily limited to second order processes. As the pressure in the source is increased third order and higher processes come into evidence; with some of the olefins we have observed some reactions as high as sixth order in pressure, although in these instances the total amount of product observed was quite small. In methane, however, at 200 microns we find several per cent $C_3H_5^+$ ions produced, and in ethylene the $C_5H_9^+$ ion at these conditions is about 10% of the reactant $C_2H_4^+$ ion. Both of these processes are necessarily at least third order in pressure.

When we have established the nature of a chemical reaction and can measure the concentration of reactants and products, we can usually obtain information about the rate of reaction. In a mass spectrometer source the number of ions is always small compared to the number of molecules present. Thus, for the reaction

$$A^+ + B \rightarrow C^+ + D \qquad (5)$$

we can write

$$\frac{(A^+)}{(A_0^+)} \approx \frac{I_{A^+}}{(I_{A_0^+})} = e^{-k_1(B)t} \qquad (9)$$

$$\frac{(C^+)}{(A_0^+)} = \frac{I_{C^+}}{I_{A_0^+}} = 1 - e^{-k_1(B)t} \qquad (10)$$

where k is reaction rate constant, t is the residence time of the primary ion in the source and the intensity (I)

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of a given ion current is assumed to be proportional to the concentration of the ion. At low values of $k_1(B)t$

$$\frac{I_{C^+}}{I_{A_0^+}} \approx k_1(B)t \tag{11}$$

Similarly, if we have a third order process such as

$$A^+ + 2D \rightarrow T^+ + F \tag{12}$$

we can write

$$\frac{I_{A^+}}{I_{A_0^+}} = e^{-k_1(B)^2 t} \tag{13}$$

$$\frac{I_{T^+}}{I_{A_0^+}} = 1 - e^{-k1(B)^2 t} \approx k_1(B)^2 t \tag{14}$$

Thus, from equation (11) a plot of the ratio of intensities of the product and reactant ions against concentration of neutral species in the source should give a straight line of slope kt if the reaction is second order. Similarly, if the reaction is third order the plot of the intensity ratio against the square of the pressure should give us a straight line of slope kt. In Figure 6 *a–b* we give plots of data for second order and third order reactions. We can compute the retention time of the primary ion in the source from our knowledge of the voltage applied to the repeller electrode, the mass of the ion, and the dimensions of the source. In our instrument the time is in the order of 10^{-6} sec. Employing kt obtained from a plot such as that in Figure 6 *a–b* and the time, we can obtain k, the rate constant for the reaction. By now the literature contains many such constants and typical values for several second and third order constants are given in Table 11. The second order reactions mostly tend to be in the order of 10^{-10} and 10^{-9} cc/molecule sec. These are very fast reactions as was mentioned previously. Similarly, the values for the third order rate constants are very great indeed, being in the order of 10^{-25} to 10^{-29} cc^2/molecule^{2}sec. For comparison, the rate constant for the recombination of nitrogen atoms in the presence of a third body is about 10^{-32} cc^2/molecule^{2}sec.

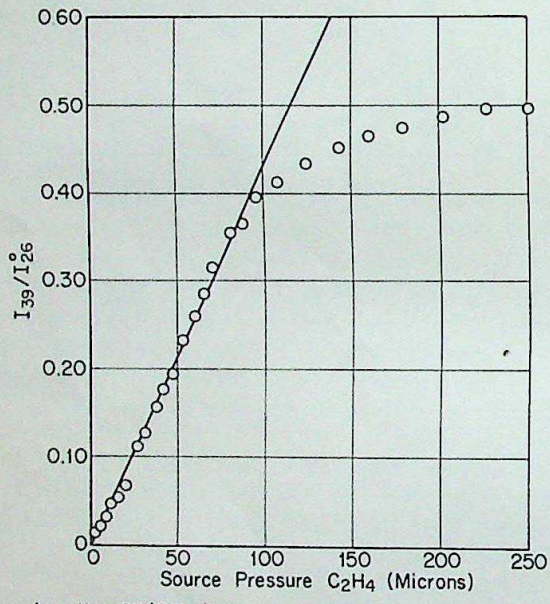


Figure 6a. Mass 39 ($C_3H_3^+$) calculated and experimental pressure plot.

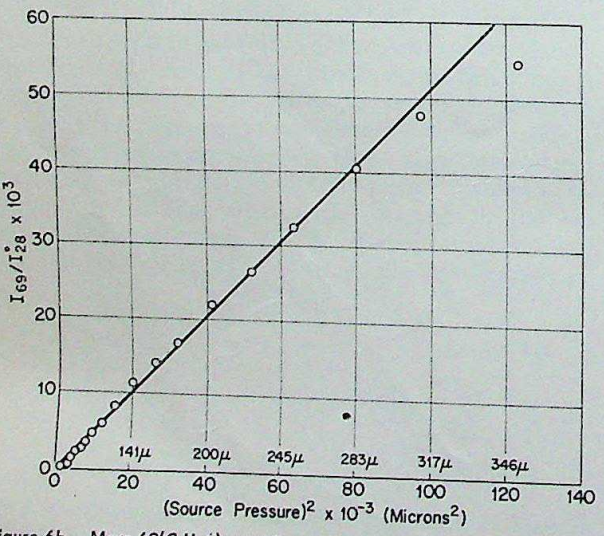


Figure 6b. Mass 69($C_5H_9^+$) experimental pressure plot.

Table 11. Rates of Ion-Molecule Reactions

	k	
Second Order Reactions	(cc/molecule sec)	Ref.
$CH_4^+ + CH_4 \rightarrow CH_5^+ + CH_3$	8.5×10^{-10}	(*6a*)
$CH_3^+ + CH_4 \rightarrow C_2H_5^+ + H_2$	8.5×10^{-10}	(*6a*)
$H_2O^+ + H_2O \rightarrow H_3O^+ + OH$	12.8×10^{-10}	(*6a*)
$H_2S^+ + H_2S \rightarrow H_3S^+ + HS$	3.0×10^{-10}	(*6a*)
$R^+ + C_3H_8 \rightarrow C_3H_7^+ + R$	2.1×10^{-10}	(*6a*)
$C_2H_4^+ + C_2H_4 \rightarrow$		
$(C_4H_8^+) \rightarrow C_3H_5^+ + CH_3$	4.6×10^{-10}	(*6a*)
$(C_4H_8^+) \rightarrow C_4H_7^+ + H$	0.5×10^{-10}	(*6a*)
$C_2H_2^+ + C_2H_2 \rightarrow C_4H_2^+ + H_2$	3.7×10^{-10}	(*6a*)
$Ar^+ + CH_4 \rightarrow ArH^+ + CH_3$	0.02×10^{-10}	(*16*)
$Ar^+ + CH_4 \rightarrow ArCH_3^+ + H$	0.0003×10^{-10}	(*16*)
$Ar^+ + CH_4 \rightarrow ArCH_2^+ + H_2$	0.0008×10^{-10}	(*16*)
$Ar^+ + CH_4 \rightarrow CH_2^+ + H_2 + Ar$	2.3×10^{-10}	(*16*)
$Ar^+ + CH_4 \rightarrow CH_3^+ + H + Ar$	9.1×10^{-10}	(*16*)
	k	
Third Order Reactions	(cc^2/molecule^2 sec)	
$Ar^+ + 2Ar \rightarrow Ar_2^+ + Ar$	2.1×10^{-28}	(*18*)
$C_2H_3^+ + 2C_2H_4 \rightarrow C_6H_5 + 3H_2$	1.7×10^{-27}	(*19*)
$C_2H_2^+ + 2C_2H_4 \rightarrow C_5H_5^+ + CH_3 + H_2$	4.3×10^{-27}	(*19*)
$C_2H_4^+ + 2C_2H_4 \rightarrow C_4H_8^+ + C_2H_4$	2.0×10^{-27}	(*19*)
$C_2H_5^+ + 2C_3H_8 \rightarrow$ Products	7.1×10^{-26}	(*20*)

Kineticists tend to think of reaction rate constants as increasing when the energy (i.e., the temperature) of the reactants increases. Ordinary chemical reactions involve an activation energy. Such reactions are usually carried out in systems having a Boltzmann energy distribution which prescribes an increase with temperature of the fraction of molecules possessing sufficient energy to react. Of course, where the reaction has no activation energy, the rate constant should not vary significantly with energy. We find that the ion-molecule reactions we have studied (which involve no activation energy) actually *decrease* markedly in rate as the relative velocities of the ion and neutral reactants increase. Stevenson and Schissler (*9*) have found some ion-molecule reactions whose rate constants were invarient with field strength; however, there are many which do vary with field strength and all of the variation is in the direction of reduced rate constants at higher field strength.

Chemi-Ionization Reactions

It has been known for many years that at some conditions the rare gases form diatomic ions. Several years ago Hornbeck and Molnar (*10*) employed a mass

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spectrometer to study the formation of rare gas diatomic ions and discovered that their appearance potentials were about 0.7 to 1.5 v below the ionization potential of the respective rare gas. This can only be interpreted as involving the reaction of an electronically excited atom with an atom in the ground state as follows

$$Ar^* + Ar \rightarrow Ar_2^+ + e \qquad (15)$$

A number of reactions of this kind have now been observed and they have been given the name "chemi-ionization" reactions. In our laboratories we have remeasured the appearance potential of various homonuclear diatomic ions obtaining good agreement with the values of Hornbeck and Molnar. In Figure 7 the ionization efficiency curve for Ar_2^+ and for Ar^+ are given. The latter is typical of curves for the direct ionization of a rare gas where the intensity rises rather rapidly after onset and reaches a plateau where it remains constant over a rather wide range of electron energies. The intensity of Ar_2^+ on the other hand rises rapidly to a maximum a few volts above its appearance potential then declines sharply. The shape of the curve is very similar to that for certain excitation processes and reinforces the conclusion that Ar_2^+ is formed from an electronically excited atom. In addition, we have studied various combinations of the rare gases and find that all of the possible heteronuclear diatomic ions are formed also. In the course of these investigations we have also studied mixtures of the rare gases with other materials and somewhat to our surprise found that quite a number of compounds of the rare gases with other materials are formed by chemi-ionization reactions. Thus, we have observed such interesting products as $XeCH_4^+$, ArN_2^+, $KrCO^+$, and XeO_2^+. Other investigators have likewise observed compounds of this kind; for example, Rudolph and Melton (*11*) have reported $XeC_2N_2^+$ presumably as a result of chemi-ionization reaction and Cermak (*12*) has reported several compounds of mercury formed by such reactions, including $HgNH_3^+$, $HgCS_2^+$, HgH_2O^+. Table 12 gives several chemi-ionization reactions.

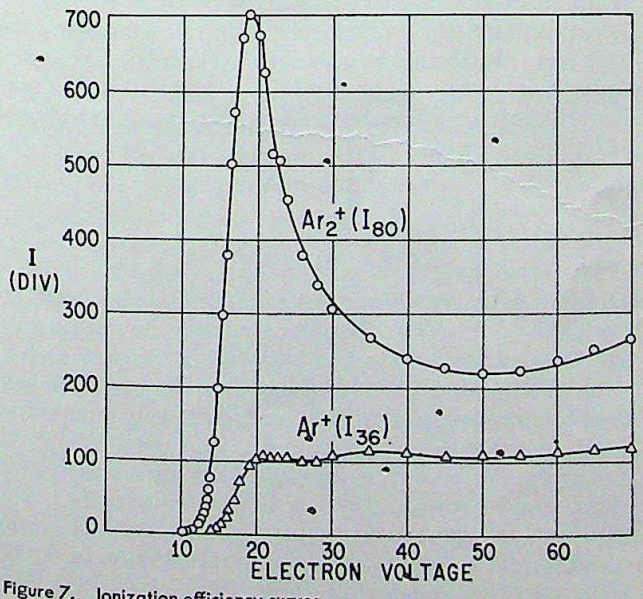


Figure 7. Ionization efficiency curves.

Because chemists, we naturally wished to know the rates of chemi-ionization processes. Unfortunately, the mass spectrometer is not well suited to the study of this problem. The difficulty is that the number of excited atoms taking part in the reaction is not directly measurable, their presence being known only by inference from the products of reaction. Nevertheless, we have undertaken the measurement of the rates of formation of several rare gas diatomic ions with moderate success. The measurement is based upon the following mechanism, taking argon as an example:

$$Ar + e \rightarrow Ar^+ + 2e \qquad k_i \qquad (16)$$

$$Ar + e \rightarrow Ar^* + e \qquad k_e \qquad (17)$$

$$Ar^* \rightarrow Ar + h\nu \qquad k_u = 1/\tau_u \qquad (18)$$

$$Ar^* + Ar \rightarrow Ar_2^+ + e \qquad k_2 \qquad (19)$$

$$Ar^+ + 2Ar \rightarrow Ar_2^+ + Ar \qquad k_3 \qquad (20)$$

Applying the steady-state criterion to Ar* gives

$$\dot{Ar}^* = \frac{k_e I(Ar)}{k_u + k_2(Ar)} \qquad (21)$$

$$\frac{d(Ar_2^+)}{dt} = k_2(Ar)(Ar^*) + k_3(Ar)^2(Ar^+) \qquad (22)$$

which readily integrates to

$$\frac{I_{Ar_2^+}}{I_{Ar^+}} = \frac{(Ar_2^+)}{(Ar^+)} = \frac{k_e}{k_i}\frac{k_2 Ar \tau_u}{(1 + k_2(Ar)\tau_u)} + k_3(Ar)^2\tau_i \qquad (23)$$

Is is assumed that ion intensities are proportional to concentration.

In equation (23) the first term on the right represents the product of diatomic ions by chemi-ionization and the second term is that for recombination by the three-body process. If we could repress one of these and measure the other we would be in a good position to obtain at least relative rate constants. Now we know that from the shape of the ionization efficiency curve given in Figure 7 the chemi-ionization process is maximized and the three-body process minimized by operating at low electron energy. Further, we know that the rates of ion-molecule reactions are surpressed by operation at high repeller field strength whereas chemi-ionization processes, which involve only neutral species, should be unaffected by field. Accordingly, we set the repeller voltage at a high value and the electron energy at a comparatively low one (near the maximum of the ionization efficiency curve) and observed the variation of relative ion intensities with pressure. If

Table 12. Chemi-Ionization Reactions

$Kr^* + Kr$	$\rightarrow Kr_2^+ + e$
$Xe^* + CH_4$	$\rightarrow XeCH_4^+ + e$
$\begin{bmatrix} Xe^* + C_2H_2 \\ C_2H_2^* + Xe \end{bmatrix}$	$\rightarrow XeC_2H_2^+ + e$
$\begin{bmatrix} Xe^* + O_2 \\ O_2^* + Xe \end{bmatrix}$	$\rightarrow XeO_2^+ + e$
$Kr^* + I_2$	$\rightarrow KrI^+ + I + e$
$Ar^* + N_2$	$\rightarrow ArN_2^+ + e$
$Kr^* + CO$	$\rightarrow KrCO^+ + e$
$N_2^* + N_2$	$\rightarrow N_4^+ + e$
$CO^* + CO$	$\rightarrow C_2O_2^+ + e$
$Ar^* + Hg$	$\rightarrow ArHg^+ + e$
$N_2^* + Hg$	$\rightarrow N_2Hg^+ + e$
$Hg^* + H_2O$	$\rightarrow HgOH_2^+ + e$
$Hg^* + CH_4$	$\rightarrow HgCH_4^+ + e$

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the three-body process is completely suppressed, equation (23) would reduce to

$$\frac{I_{Ar_2^+}}{I_{Ar^+}} = \frac{k_e k_2(Ar)\tau_u}{k_i(1 + k_2 Ar\tau_u)} \qquad (24)$$

Inverting equation (24) gives

$$\frac{I_{Ar^+}}{I_{Ar_2^+}} = \frac{k_i}{k_e} + \frac{k_i}{k_e k_2(Ar)\tau_u} \qquad (25)$$

One would expect from equation (24) that the curve obtained by varying the pressure would rise rapidly with pressure and at high pressures tend to saturate. Figure 8 shows that the results agreed with our expectations. Further, it will be observed from equation (25) that a plot of $I_{Ar^+}/I_{Ar_2^+}$ against the reciprocal of pressure should give a straight line with intercept k_i/k_e and slope $(k_i/k_e k_2\tau_u)$. Figure 9 again bears this out quite well. The intercept is in fact the ratio of the number of atomic ions to reacting excited atoms formed by electron impact and thus we have a measure of the relative intensities of reactants present in the source. From this and the slope of the line we obtain a value of $k_2\tau_u$ where k_2 is the rate constant for the chemi-ionization reaction and τ_u is the lifetime of the excited atoms undergoing reactions. Unfortunately, we have no way of measuring τ_u and so we have no way of obtaining k_2. We do know that τ_u can be no greater than about 10^{-6} sec as limited by the mean time required by the atoms to diffuse to the wall where they discharge their energies. Similarly, their lifetime might be as short as about 10^{-8} sec as limited by the time required for radiation. Probably a lifetime between 10^{-8} and 10^{-7} sec is reasonable. From the data in Table 13 we conclude that using the maximum value of τ leads to a value of the rate constant for the chemi-ionization reaction that is comparable to that of ion-molecule reactions. On the other hand, using the smallest value for τ_u we obtain a rate constant that is extremely large. In fact, expressed in terms of cross section, this would be in the order of 5000 Å^2. Even with 10^{-7} sec the rate constant is very large indeed.

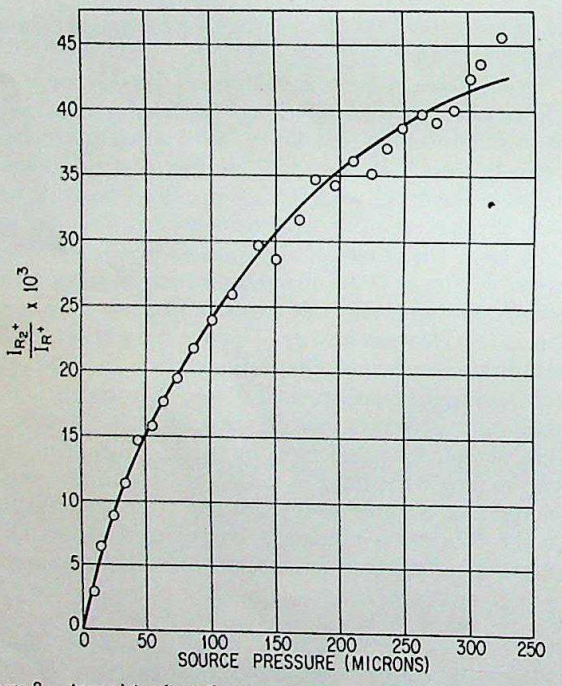


Figure 8. Argon intensity ratio versus source pressure.

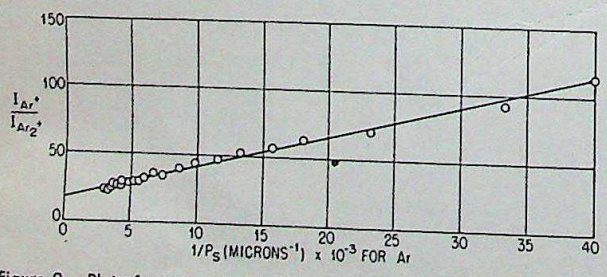


Figure 9. Plot of argon rate data according to equation (25).

Table 13. Rates of Chemi-Ionization Reactions (50 v/cm field strength)

Rare gas	Electron energy (v)	k_e/k_i	$10^{16}k_2\tau_u$	Assumed τ_u	k_2
Ar	15	0.055	3.6	10^{-6}	3.6×10^{-10}
				10^{-7}	3.6×10^{-9}
				10^{-8}	3.6×10^{-8}
Ne	20	0.010	11.6	10^{-6}	11.6×10^{-10}
				10^{-7}	11.6×10^{-9}
				10^{-8}	11.6×10^{-8}
He	22	0.064	0.6	10^{-6}	0.6×10^{-10}
				10^{-7}	0.6×10^{-9}
				10^{-8}	0.6×10^{-8}

By altering the conditions in the source in such a way as to minimize chemi-ionization and maximize ion-molecule reactions we have been able to measure the specific rate of the three-body recombination for the formation of the Ar_2^+ and Ne_2^+. The rate constants are 2.1×10^{-28} and 2.0×10^{-29} cc^2/molecule^2 sec, respectively. Again, these represent quite fast reactions although they are several orders of magnitude slower than some of the third order processes observed with hydrocarbons.

Table 12 includes chemi-ionization reactions of nitrogen and carbon monoxide to form N_4^+ and $C_2O_2^+$. Munson, Field, and Franklin (*13*) have studied chemi-ionization reactions of mixtures of these materials with the rare gases also. They find that argon, krypton, and xenon react with both N_2 and CO to form compound ions such as ArN_2^+ and $KrCO^+$ by chemi-ionization processes, the excited species in all cases being the rare gas. In the argon–nitrogen system the argon was found to enhance the production of N_4^+ and it was concluded that the following mechanism accounted for the behavior observed:

$$Ar^* + N_2 \rightarrow ArN_2^+ + e \qquad (26)$$

$$Ar^+ + Ar \rightarrow Ar_2^+ + e \qquad (27)$$

$$ArN_2^+ + N_2 \leftrightarrows N_4^+ + Ar \qquad (28)$$

Similar behavior was observed with the systems Kr–CO and Ar–CO. Thus we find the rare gases serving as catalysts for the formation of N_4^+ and $C_2O_2^+$.

It will be obvious from the material presented here that chemi-ionization is a comparatively unstudied field of chemical reactions and one that needs and justifies investigation. The importance of such reactions in the chemical transformations brought about by radiation and by electric discharges is evident. They are also thought to be the means of ion formation in flames although the responsible reactants have not been

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identified. There is reason to think that charge transfer and ionization reactions may occur in the upper atmosphere although this is largely speculative now. The problem, however, is of great interest and no doubt will be investigated.

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Temperature Dependence of Equilibrium

A first experiment in general chemistry

Recently increasing attention has been given to the problem of introducing thermodynamic concepts into the freshman chemistry course. One of the most useful results of thermodynamic analysis is the expression for the temperature dependence of the equilibrium constant:

$$\ln \frac{K_2}{K_1} = -\frac{\Delta H^\circ}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

where K_1 and K_2 are the equilibrium constants at the temperatures T_1 and T_2, ΔH° is the standard enthalpy change for the reaction, and R is the gas constant. This valuable equation applies not only to chemical equilibria; it also forms the basis for understanding the temperature dependence of vapor pressure, boiling point elevation, and freezing point depression phenomena. Its derivation need not involve the Gibbs-Helmholtz equation. Starting from the fundamental relations which relate the equilibrium constant to the standard free energy change, ΔF°, the standard entropy change, ΔS°, and the standard enthalpy change

$$\Delta F^\circ = \Delta H^\circ - T\Delta S^\circ$$

$$\Delta F^\circ = -RT \ln K$$

we can write

$$\ln K = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R}$$

This equation says that $\ln K$ is a linear function of $1/T$ if ΔH° and ΔS° are independent of temperature. The temperature dependence of ΔH° and ΔS° can be expressed as

$$\Delta H^\circ_T = \Delta H^\circ_{298} + \int_{298}^{T} \Delta C_p dT$$

$$\Delta S^\circ_T = \Delta S^\circ_{298} + \int_{298}^{T} \frac{\Delta C_p}{T} dT$$

where ΔC_p is the difference in the heat capacities of products and reactants. Clearly if ΔC_p is very small, ΔH° and ΔS° are both virtually independent of temperature and we can write

$$\ln K_2 = -\frac{\Delta H^\circ}{RT_2} + \frac{\Delta S^\circ}{R}$$

$$\ln K_1 = -\frac{\Delta H^\circ}{RT_1} + \frac{\Delta S^\circ}{R}$$

and

$$\ln \frac{K_2}{K_1} = -\frac{\Delta H^\circ}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

It is very desirable to have students demonstrate the validity of this equation in the laboratory. For such an experiment we require a reaction which involves "ideal" reagents, and whose equilibrium constant can be determined rapidly at several temperatures without the

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use of a thermostat. The dissolution of naphthalene in diphenylamine meets all these specifications. Since the reaction can be written as

naphthalene (pure solid) ⇆ naphthalene (solution, conc X)

the equilibrium constant is $K = X$, where X is the mole fraction of naphthalene in a solution which is in equilibrium with pure solid naphthalene. The temperature dependence of the equilibrium can be found by weighing out naphthalene and diphenylamine to form mixtures of known composition, melting them in a water bath, and determining the temperature at which naphthalene first precipitates by the cooling curve method. A plot of log X as a function of the reciprocal temperature yields a straight line of slope $-\Delta H°/2.3\,R$. It is easy to see that the $\Delta H°$ determined this way is the enthalpy of fusion of naphthalene. If the reaction is written as two steps

pure solid naphthalene ⇆ pure liquid ⇆ solution

it is clear that the enthalpy change of the first step is the enthalpy of fusion of naphthalene, while the enthalpy change of the second step is zero, since the solution is ideal.

The Experiment

Data for cooling curves (temperature *vs.* time) are obtained on the pure solvent, naphthalene, and on at least four solutions of diphenylamine in naphthalene in the range of 1 to 0.4 mole fraction naphthalene. Conventional procedures can be used; we suggest having the students plot each cooling curve (temperature readings every 30 seconds) to identify the temperature at which the slope changes as well as having them attempt to identify the temperature at which the first solid appears.

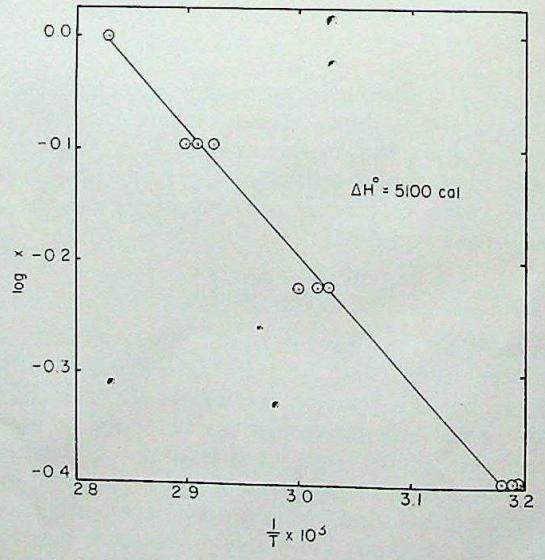
A 20-gram sample of solvent naphthalene is sufficient, if weighings are made to 0.10 gram. The addition of successive samples of solute to the same amount of solvent simplifies the procedure. Diphenylamine can be added until the naphthalene mole fraction is about 0.4; more diphenylamine will not remain in solution. The four values of log X as a function of $1/T$ are plotted and the enthalpy of fusion of naphthalene is evaluated from the slope. Typical student results are shown in the drawing. Generally the answers fall within ±500 calories of the accepted value of 4600 calories.

Making Thermodynamics Meaningful

The simplicity of the solubility equilibrium makes it an excellent device for pointing out the difference between $\Delta F°$ and ΔF. The standard free energy change, $\Delta F°$, is the difference in free energy between the *pure* liquid naphthalene and the pure solid, while ΔF is the difference in free energy between the naphthalene in solution at a concentration X and the pure solid. Defined in this way, $\Delta F°$ is a function of temperature, and is zero only at the freezing point of pure naphthalene. On the other hand, the condition for equilibrium at all temperatures is that $\Delta F = 0$. This means that at equilibrium, $T\Delta S = \Delta H$, or if $\Delta H°$ is independent of temperature, $T\Delta S = \Delta H°$. Thus in order for equilibrium to occur at a lower temperature than the melting point of pure naphthalene, the entropy change associated with the solution process, ΔS, must be greater than $\Delta S°$, the entropy of fusion. By using the molecular interpretation of entropy, we can say that the entropy of fusion, $\Delta S°$, is a measure of the increased freedom of movement which the molecules in the pure liquid have compared with those in the solid. Equivalently we can say that the entropy of fusion measures the increased disorder of the pure liquid compared with the solid, since if molecules have available to them more positions and types of motion, we are less able to predict their behavior; thus we characterize them as more disordered. Now if a solid has the opportunity to "melt" or dissolve not into its pure liquid phase, but into another liquid, the gain in the number of positions available to its molecules is even greater, and increases as the solution formed becomes more dilute. That is, solute molecules in a dilute solution have available to them a greater number of positions than they would in a more concentrated solution or in a pure liquid. Consequently, ΔS, the entropy associated with the process

pure solid state → solute in solution, conc X

increases as X decreases, and thus the condition for equilibrium between the solid and its ideal solution, $T\Delta S = \Delta H°$, can be satisfied at lower and lower temperatures.



Typical student data for the temperature dependence of the solubility of naphthalene in diphenylamine. The slope of the line corresponds to $\Delta H° = 5100$ calories.

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The Valence-Shell Electron-Pair Repulsion (VSEPR) Theory of Directed Valency

Directed valency is conventionally explained in terms of the directional character of p and d orbitals (*1*). The explanation of the angular shape of the water molecule as resulting from bond formation by two oxygen $2p$ orbitals that make an angle of 90° to each other is to be found in most freshman texts. The difficulties encountered in the direct application of this theory to carbon and the consequent introduction of the concept of hybridization are also very familiar. The limitations of this theory and in particular the idea that hybrid orbitals are a description of rather than an explanation for molecular shape are, however, generally not discussed in elementary introductions to the subject. For example, in the case of five-coordination in which the bonding orbitals are described as a set of five $sp^3\ d$ hybrid orbitals, it is necessary to make an arbitrary choice of the single d-orbital; the $d_{x^2-y^2}$ orbital gives a set of hybrids corresponding to a square pyramid shape, while the d_{z^2} orbital gives a set of hybrids corresponding to a trigonal bipyramid shape.

In the early development of the simple valence-bond picture little attention was paid to the effects of lone-pairs of electrons on molecular shape. As long ago as 1940, however, Sidgwick and Powell (*2*) drew attention to the fact that the shape of a molecule could be accounted for in terms of the arrangement of all the electron-pairs (both bonding and non-bonding pairs) in the valence-shell of the central atom, a given number of electron pairs always having the same arrangement. Since that time the importance of lone pairs has been stressed by a number of authors. Lennard-Jones and Pople (*3*) pointed out that water and ammonia could be described in terms of a set of sp^3 hybrid orbitals on the central atom which are occupied by two bonding and two lone pairs of electrons in water and three bonding and one lone pair of electrons in ammonia. These ideas were developed further by Mellish and Linnett (*4*) who consider that a lone pair, being under the influence of only one nucleus rather than two, occupies more of the surface of an atom than the bonding pairs and that therefore the angle between the bonding pairs is reduced to less than the tetrahedral angle as in the case in water and ammonia. Fowles (*5*) has summarized some of the effects of lone-pair electrons on bond lengths and bond angles and other molecular properties.

Gillespie and Nyholm (*6*) have shown how the ideas of Sidgwick and Powell (*2*) can be combined with the more recently developed ideas on lone pairs to account in a qualitative manner for the general shapes and bond angles of most inorganic molecules. These authors pointed out that the arrangements of electron pairs in a valence shell could be regarded as arising from the mutual interactions between the electron pairs which are a consequence of both electrostatic forces and the operation of the Pauli exclusion principle. The purpose of the present paper is to review recent developments of these ideas and to show that a very satisfactory understanding of a large number of the features of the structures of inorganic molecules can be understood and rationalized in terms of the repulsions between the electron pairs in valence shells without making any use of the concept of hybrid orbitals. The paper attempts to give a consistent discussion of molecular shape and stereochemistry from the point of view of this theory only. Discussions of molecular shape from alternative, although sometimes related, points of view have been given in other recent papers in THIS JOURNAL (*7–9*).

Basic Ideas

The theory proposes that the stereochemistry of an atom is determined primarily by the repulsive interactions between the electron pairs in a valence shell. The electrons in a valence shell are regarded as occupying essentially localized orbitals that are oriented in space around the nucleus and the completed inner electron shells so that their average distance apart is maximized (*2, 6, 10, 11*). This may be regarded as a consequence of the operation of the Pauli exclusion principle according to which electrons of the same spin tend to keep as far apart as possible (*6, 10–12*). Thus two electrons of the same spin have a maximum probability of being found on opposite sides of the nucleus, three electrons at the corners of an equilateral triangle and four at the corners of a tetrahedron. In the valence shell of an atom in a molecule there are generally equal numbers of electrons of opposite spin. Thus for the common case of a valence shell of eight electrons, there will be a set of four electrons of parallel spin having a maximum probability of being found at the corners of a tetrahedron, and a second set of electrons of opposite spin also having a maximum probability of being found at the corners of a second tetrahedron. This would, for example, be the situation for Ne, F^-, $O^=$ and N^{3-}. When one or more protons, or other positive ions combine with these ions to form neutral molecules two electrons of opposite spin are attracted towards each other and the two tetrahedra are brought into coincidence. There are then four essentially localized electron-pairs, i.e., four tetrahedrally directed orbitals each containing an electron-pair. These tetrahedral orbitals are approximately equivalent to the sp^3-orbitals of valence-bond theory.

The tendency of electron pairs in a valence-shell to adopt an arrangement which maximizes their average distance apart may be regarded as arising from repulsive interactions between the electron-pairs. Each electron

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pair occupies as much of the available nucleus and inner shells as it can keeping other electron-pairs out of this space. In the case of four such electron-pairs the available space may be regarded as being divided into four tetrahedrally directed segments each of which is occupied by an electron-pair. The repulsions that we are considering between electron-pairs are essentially the same as those that operate between inert gas atoms, or any pair of non-bonded atoms with filled valence shells. Although these non-bonded repulsions may sometimes be of importance in determining molecular structure, the valence-shell electron-pair repulsion theory—henceforth called the VSEPR theory—regards the repulsions between the bonding and the non-bonding electron-pairs in the valence-shell of the central atom as being the most important factor in determining the stereochemistry, the interactions between the non-bonding electron-pairs on different ligands being of relatively minor importance except in special situations. This repulsion may be called a van der Waals repulsion, an exchange repulsion, or a spin-correlation repulsion. The repulsive interaction between inert gas atoms may be very approximately represented by a potential function which involves a $1/r^n$ term where n has a fairly large value, e.g., 12, as in the Lennard-Jones potential function. It is assumed that the interaction between the electron-pairs in a valence-shell may be approximately represented by a similar potential function. An interaction of this form means that when the overlap between two orbitals is very small they interact to a negligible extent, but as the overlap increases their repulsive interaction increases very rapidly.

It is evident from general elementary considerations, and it can also be proved rigorously (*6*, *13*, *14*), that the most probable arrangements of two, three, four, and six electron-pairs are collinear, equilateral triangular, tetrahedral, and octahedral, respectively. For five electron pairs the trigonal bipyramid and the square pyramid are equally probable for $n = \infty$ but for $n < \infty$ the trigonal bipyramid has a slightly greater probability than the square pyramid (*14*, *15*).

Higher coordination numbers can be considered in the same manner but they will not be further discussed in this article (*11*, *16*).

In the case of transition metals there is in general an incomplete *d*-shell beneath the valence-shell which will not necessarily have the spherical symmetry of a completed shell. In such cases it is necessary to consider the interaction of the valence-shell electron-pairs with the non-spherical *d*-shell as well as with each other. In the following discussion we will consider only molecules of the non-transition elements and transition elements with symmetrical d^0, d^5 (spin-free) and d^{10} shells.

Shapes of Molecules

Each of the preferred arrangements of a given number of electron-pairs can in general give rise to several molecular shapes depending on the relative numbers of bonding-pairs and lone-pairs. The following terminology is useful: A is a central atom, X is a ligand and E is a lone-pair. Thus in a singly bonded molecule AX_mE_n there are $m + n$ electron-pairs in the valence-shell of which m are bonding pairs and n are non-bonding or lone-pairs. The shape of the molecule is determined by the preferred arrangement of the $m + n$ electron-pairs. Or, if we consider the electron-pairs to each occupy a two-electron orbital, the shape is determined by the arrangement of the $m + n$ orbitals. The various possible molecular shapes that can be obtained in this way are given in Table 1 and Figure 1. Predicted shapes for the recently discovered molecule XeF_4 and the XeF_2 are included. In the cases of AX_4 E, AX_3E_2, AX_2E_3, and AX_4E_2 molecules there are possible alternative positions for the lone-pairs. In fact they are always found in the equatorial positions in AX_4E, AX_3E_2, and AX_2E_3 molecules and in the *trans* position in AX_4E_2 molecules as shown in Figure 1. The reason for this is discussed later.

These arguments can be readily extended to include molecules in which there are one or more ligands bonded to the central atom by double or triple bonds. In such a molecule the electron-pairs are not all free to take up one of the preferred arrangements of Table 1 because

Table 1. Shapes of Molecules of the Non-Transition Elements and of d^0, d^5 (Spin-free) and d^{10} Transition Elements

2 Electron-pair valence-shells: linear
AX_2 coordination: linear
Hg_2Cl_2, $HgCl_2$, $HgBr_2$, HgI_2, $CdCl_2$, $CdBr_2$, CdI_2, ZnI_2 $Zn(CH_3)_2$, $Cd(CH_3)_2$, $Hg(CH_3)_2$, $Ag(CN)_2^-$, $Au(CN)_2^-$, $(AgCN)_x$, $(HgO)_x$
3 Electron-pair valence-shells: triangular
AX_3 coordination: triangular
BF_3, BCl_3, BI_3, $B(CH_3)_2F$, GaI_3, $In(CH_3)_3$, $[Cu(CN)_2^-]_n$
AX_2E coordination: V-shaped
$SnCl_2$, $SnBr_2$, SnI_2, $PbCl_2$, $PbBr_2$, PbI_2
4 Electron-pair valence-shells: tetrahedral
AX_4 coordination: tetrahedral
$[BeCl_2]_n$, $[Be(CH_3)_2]_n$, BeX_4^{--}, BX_4^-, CX_4, NX_4^+, $OBe_4(CH_3CO_2)_6$, $OZn_4(CH_3CO_2)_6$, BeO, ZnO, OCu, OAg, OPd, OPt, Al_2Cl_6, $Al_2(CH_3)_6$, SiX_4, GeX_4, SnX_4, PbX_4, AsX_4^+, CuCl, CuBr, CuI, ZnX_4^{2-}, HgX_4^{2-}, $TiCl_4$, $TiBr_4$, $ZrCl_4$, $ThCl_4$, $FeCl_4^-$
AX_3E coordination: trigonal-pyramidal
NX_3, OH_3^+, PX_3, AsX_3, SbX_3, P_4O_6, As_2O_3, As_4O_6, Sb_2O_3, Sb_4O_6, $[A\ O_2^-]_n$, As_2S_3]
AX_2E_2 coordination: V-shaped
OX_2, SX_2, SeX_2, TeX_2
5 Electron-pair valence-shells: trigonal-bipyramidal
AX_5 coordination: trigonal-bipyramidal
PCl_5, PF_5, PF_3Cl_2, $SbCl_5$, $Sb(CH_3)_3Cl_2$, $NbCl_5$, $NbBr_5$, $TaCl_5$, $TaBr_5$, V_2O_5, VO_3^-, Zn(terpyridyl)Cl_2, Zn(acetylacetone)$_2H_2O$
AX_4E coordination: irregular tetrahedral
SF_4, SeF_4, R_2SeCl_2, R_2SeBr_4, R_2TeCl_2, R_2TeBr_2, $TeCl_4$
AX_3E_2 coordination: T-shaped
ClF_3, BrF_3, $C_6H_5ICl_2$
AX_2E_3 coordination: linear
ICl_2^-, I_3^-, XeF_2
6 Electron-pair valence-shells: octahedral
AX_6 coordination: octahedral
SF_6, SeF_6, TeF_6, MoF_6, WF_6, WCl_6, S_2F_{10}, F_5SOF, $F_5SO_2SF_5$, $Te(OH)_6$, $(NbCl_5)_2$, PCl_3^-, PF_6^-, $Sb(OH)_6^-$, SbF_6^-, AsF_6^-, $(SbF_5)_n$, SiF_6^{2-}, $Sn(OH)_6^{2-}$, $SnCl_6^{2-}$, $PbCl_6^{2-}$, AlF_6^{3-}, TaF_6^-, NbF_6^-, VF_6^-, $TiCl_6^{2-}$, FeF_6^{3-}
AX_5E coordination: square-pyramidal
BrF_5, IF_5
AX_4E_2 coordination: square-planar
ICl_4^-, I_2Cl_6, BrF_4^-, $ISbCl_8$, XeF_4

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the two electron-pairs of a double bond and the three pairs of a triple bond are constrained to keep close together. From the point of view of their effect on the stereochemistry of a molecule the two electron-pairs of a double bond are best considered as occupying one four-electron orbital and the three electron-pairs of a triple bond as occupying one six-electron orbital. The general shape of a molecule AX_mE_n is then determined by the value of $m + n$ where m is the number of ligands X or the number of bonding orbitals, allowing one four-electron orbital for a double bond and one six-electron orbital for a triple bond. Various possible molecular shapes for molecules containing double-bonds are given in Table 2.

Bond Angles and Bond Lengths

Many of the finer details of molecular shapes can be understood on the basis of the following related postulates concerning interactions between the valence-shell electron-pairs.

(1) **Non-bonding electron-pairs repel adjacent electron-pairs more strongly than bonding electron-pairs.** Because they are under the influence of only one nucleus the two electrons of a non-bonding pair occupy a rather fatter and less confined orbital than the electrons of a bonding-pair which are under the influence of two nuclei (Fig. 2). Hence the orbital occupied by a non-bonding electron-pair will overlap with neighboring orbitals more extensively and therefore will repel the electrons in these neighboring orbitals more strongly than an electron-pair in a bonding orbital. Thus lone-pair electrons will tend to move apart and to squash bonding electron-pairs together. The repulsions between electron-pairs in a valence-shell decrease in the order lone-pair–lone-pair > lone-pair–bond-pair > bond-pair–bond-pair. In the series CH_4, NH_3, H_2O the successive replacement of bonding electron-pairs by lone-pairs causes the bond angle to decrease from 109.5° in CH_4 to 107.3° in NH_3 and to 104.5° in H_2O. In general NX_3 and OX_2 have bond angles less than the tetrahedral angle when X is singly-bonded carbon (aliphatic), nitrogen, oxygen, or fluorine due to the greater repulsion exerted by the lone-pair(s).

In some molecules in which the central atom has a valence-shell of five or six electron pairs there are possible alternative positions for lone-pairs that would give rise to different molecular shapes. The lone-pairs will tend to occupy those positions in the molecule in which their repulsive interactions with other electron-pairs are minimized and since they repel each other more strongly than they repel bond-pairs they will occupy *trans* rather than *cis* positions in an octahedral arrangement of six electron pairs. In a trigonal bipyramid arrangement of five electron-pairs the axial pairs have three neighboring pairs at 90° while the equatorial pairs have only two neighboring pairs at 90° and two more at 120°. Since

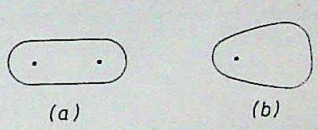


Figure 2. Diagrammatic representation of the approximate shapes of (a) a bonding orbital and (b) a non-bonding or lone-pair orbital.

the repulsion between neighboring electron-pairs falls off very rapidly with the angle between them, it is reasonable to assume that the interaction between electron-pairs at 120° is negligibly small. Hence, it is clear that the lone-pairs will tend to occupy the equatorial rather than the axial positions in these molecules, giving the shapes shown in Figure 1 rather than the possible alternative shapes with one or more of the non-bonding pairs in an axial position (*15*).

(2) **The repulsions exerted by bonding electron-pairs decrease with increasing electronegativity of the ligand.** This can be regarded as an extension of (1). An unshared pair has no ligand and therefore occupies a larger, "fatter" orbital than a bonding pair; it may be regarded as a bonding pair attaching a ligand of zero electronegativity. Any ligand attracts the bonding electron-pair to some extent contracting the orbital and drawing it in toward itself. The greater the electronegativity of the ligand the more contracted is the bonding electron orbital and the nearer to the ligand is the average position of the bond-pair (*6*, *12*). Hence, as the electronegativity of the ligand increases, the amount of overlap between the bonding orbital and neighboring orbitals decreases. In agreement with this idea it is found that the bond angle in OF_2 (103.2°) is less than that in H_2O (104.5°) and the bond angle in NF_3 (102°) is less than in NH_3 (107.3°) (Table 3). In the series PCl_3 (100°), PBr_3 (101.5°), PI_3 (102°) the bond angle increases as the electronegativity of the halogen decreases. A similar variation in bond angle is

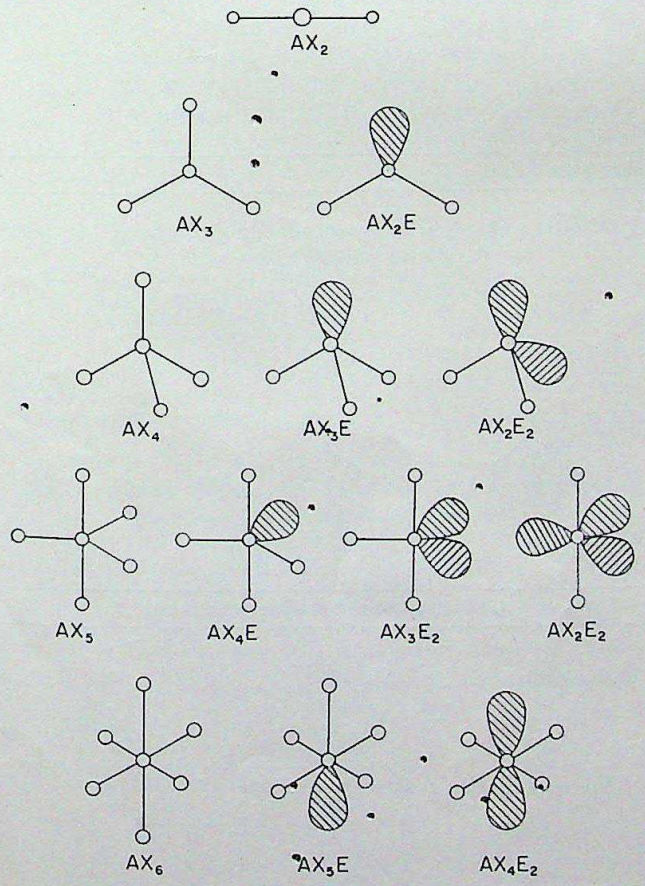


Figure 1. General shapes of molecules of the non-transition elements and of d^0, d^5 (spin-free) and d^{10} transition elements.

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found in the series $AsCl_3$ (98.4°), $AsBr_3$ (100.5°) and AsI_3 (101.5°) (Table 4)

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(3) **Multiple-bond orbitals repel other orbitals more strongly than single bond orbitals.** The repulsions exerted by multiple bond orbitals on other orbitals decrease in the order triple bond > double bond > single bond. This generalization may be regarded as a further extension of the ideas already discussed in (1) and (2). Triple bond orbitals which contain three electron-pairs are necessarily larger and therefore overlap more with nearby orbitals than double bond orbitals which contain only two electron-pairs, and double bond orbitals are in turn generally larger than single bond orbitals. Thus angles involving multiple bonds tend to be larger than angles involving single bonds only. Some examples are given below. For AX_3 molecules the "ideal" bond angle is 120° but when one of the ligands is a double-bonded atom the angles involving this ligand are always greater than 120° and the other angles correspondingly smaller (Table 5). For AX_4 molecules the "ideal" bond angle is 109.5° but when one of the ligands is a double-bonded oxygen or

Table 3. Bond Angles (in degrees) in the Hydrides of Groups V and VI

NH_3	107.3	H_2O	104.5
PH_3	93.3	H_2S	92.2
AsH_3	91.8	H_2Se	91.0
SbH_3	91.3	H_2Te	89.5

Table 4. Bond Angles (in degrees) for Group V Halides

NF_3	PF_3	AsF_3	
102.1	104	102	
	PCl_3	$AsCl_3$	$SbCl_3$
	100.0	98.4	99.5
	PBr_3	$AsBr_3$	$SbBr_3$
	101.5	100.5	97
	PI_3	AsI_3	SbI_3
	102	101	99

Table 2. Shapes of Molecules Containing Double-Bonds

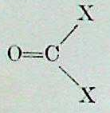
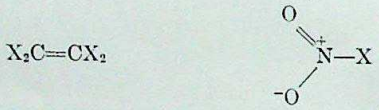
2 Orbital valence-shells : linear

AX_2 coordination : linear

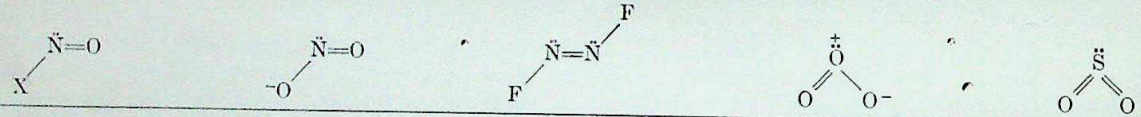
$O{=}C{=}O$ $\quad$ $O{=}\overset{+}{N}{=}O$ $\quad$ $H_2C{=}C{=}CH_2$

3 Orbital valence-shells : triangular

AX_2 coordination : triangular

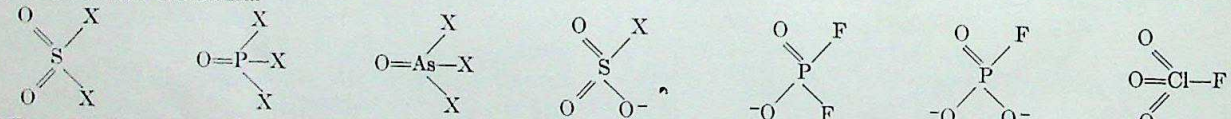



AX_2E coordination : V-shaped

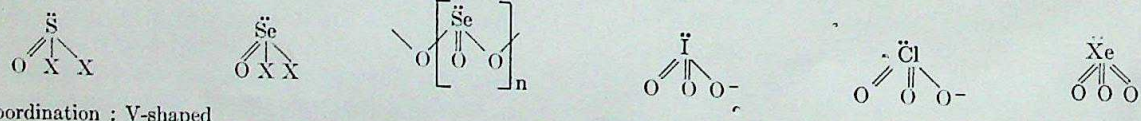


4 Orbital valence-shells : tetrahedral

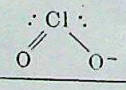
AX_4 coordination : tetrahedral



AX_3E coordination : trigonal pyramidal

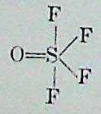


AX_2E_2 coordination : V-shaped

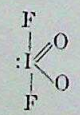


5 Orbital valence-shells : trigonal bipyramidal

AX_5 coordination : trigonal bipyramidal



AX_4E coordination : irregular tetrahedral

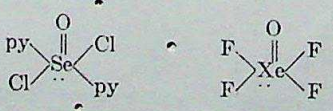


6 Orbital valence-shells : octahedral

AX_6 coordination : octahedral

$O{=}I(OH)_5$

AX_5E coordination : square pyramidal



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sulfur atom the angles involving this ligand are always larger than the other bond angles (Table 6). In AX_4 molecules containing two double-bonds the largest angle is always found to be the angle between the double bonds (Table 6). Again, in AX_3E molecules containing one double bond, the angle involving this bond is always larger than the other angles (Table 6).

(4) **Repulsions between electron-pairs in filled shells are larger than those between electron-pairs in incompletely filled shells.** The orbitals in a filled shell effectively occupy all the available space. Any influence tending to reduce the angle between the orbitals will cause appreciable orbital overlap and hence will be strongly resisted. The orbitals in an incompletely filled shell however do not occupy all the available space and they are therefore more susceptible to factors which can reduce the angle between the orbitals as some distortion of the angles between the electron pairs can occur without causing any appreciable overlap (*17*).

The valence-shells of the elements of the first row of the periodic table, in particular B, C, N, O, and F are completely filled by four electron-pairs. Thus quite generally for AX_4 molecules where A is a first row element and for AX_3 E and AX_2E_2 molecules where X is also a first row atom the bond angles are always within a few degrees of the ideal angle of 109.5°.

The elements of the second short period of the periodic table (Na-Cl), however, can in principle have up to nine electron-pairs in their valence-shell. In fact, for reasons which are not completely understood, the valence-shells of these elements are effectively completed by fewer electron pairs. If all the electron pairs are unshared as in argon, the maximum number appears to be four, but when all the electron-pairs are shared the maximum number appears to be six as in PF_6^- and SF_6. As might be expected we find the highest coordination numbers with the most electronegative elements, since these cause the bonding pairs to occupy the most contracted orbitals and therefore more of them can be packed around the central atom. Thus, for these elements it is reasonable to assume that bonding electron-pairs do not interact with each other very strongly until the angle between them is the same as in the octahedron, i.e., 90°. Thus in passing from SiH_4 to PH_3 the greater repulsion exerted by the lone-pair in PH_3 causes a much greater distortion of the bond angle (Table 3) than the lone-pair does in ammonia, because in phosphine interaction between the bonding-pairs does not begin to be appreciable until the bond-angle approaches 90°. In NH_3, however, there is already appreciable interaction between the bonding-pairs at the tetrahedral angle. The repulsions exerted by the two lone-pairs in H_2S would be expected to make the bond angle approach even more closely to 90° as is indeed observed. The shape of the H_2S molecule is closely related to that of SO_2F_2; the double-bond orbitals of SO_2F_2 replace the lone-pairs of H_2S (Fig. 3).

Table 5. Bond Angles (in degrees) for Some AX_3 Molecules Containing Double Bonds

$X_2C{=}O$	XCX	XCO	$X_2C{=}CX_2$	XCX	XCC
F_2CO	112.5	123.2	$(CH_3)_2C{=}C(CH_3)_2$	109	125
Cl_2CO	111.3	124.3	$(CH_3)_2C{=}CH_2$	109	125
H_2CO	118	121			
$(NH_2)_2CO$	118	121			

Table 6. Bond Angles (in degrees) in AX_4 and AX_3E Molecules Containing Double Bonds

	XPX		XPX
POF_3	102.5	PSF_3	100.3
$POCl_3$	103.6	$PSCl_3$	100.5
$POBr_3$	108	$PSBr_3$	106
	XSX		OSO
F_2SO_4	96.1		124
Cl_2SO_2	112.2		119.8
$(NH_2)_2SO_2$	112.1		119.4
$(CH_3)_2SO_2$	115		125
	XSX		XSO
F_2SO	92.8		106.8
Br_2SO	96		108
$(CH_3)_2SO$	100		107
$(C_6H_5)_2SO$	97.3		106.2
$SeOCl_2$	106		114

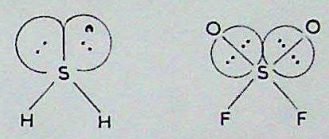
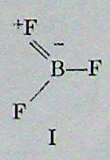


Figure 3. Approximately tetrahedral arrangement of two lone-pair orbitals and two bond orbitals in H_2S and two double-bond orbitals and two single bond orbitals in SO_2F_2

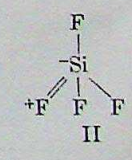
When the valence-shells of P and S are filled with six electron-pairs the bond angles do not differ significantly from 90° as observed, for example, in S_2F_{10} and SF_5OF (*18*, *19*).

With decreasing electronegativity of the central atom the bonding electron-pairs move closer to the ligands thus further decreasing their interaction and therefore the bond angle decreases slightly from H_2S to H_2Se and from PH_3 to AsH_3.

(5) **When an atom with a filled valence-shell and one or more unshared electron-pairs is bonded to an atom with an incomplete valence-shell there is a tendency for the unshared electron-pairs to be transferred from the filled shell to the incomplete shell** (17). This may be regarded as a consequence of the repulsions between electron-pairs in the filled shell being considerably larger than the repulsions between the electron-pairs in the incomplete shell. This effect causes the bonds in fluorides such as BF_3 and SiF_4 to be shorter than expected for single bonds. These bonds have considerable double-bond character as a consequence of the delocalization of the fluorine unshared electron-pairs into the incomplete valence-shell of the central atom, i.e., there are important contributions from resonance structures such as (I) and (II). This effect



I



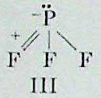
II

also has a considerable influence on the shapes of molecules. In the series of molecules PF_3, PCl_3, PBr_3 and PI_3 and AsF_3, $AsCl_3$, $AsBr_3$ and AsI_3 it might be expected, because of the decreasing electronegativity of the halogen atom, that the bond angle would increase steadily from the fluoride to the iodide. The expected

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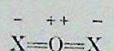
increase in bond angle is observed from the chloride to the iodide but in both cases the fluoride is anomalous having the largest rather than the smallest angle (Table 4). This may be attributed to the effect described above. The unshared electron-pairs on the fluorine have a strong tendency to delocalize into the incomplete shell of the central atom, thereby giving the bonds some double-bond character. Because of the consequent increased size of the bonding orbitals, they repel each other more strongly; and the bond angle increases accordingly. For the other halides the halogen atoms have incomplete shells and so there is little tendency for their electron-pairs to delocalize into the incomplete shell of the central atom and hence there is little or no double-bond character in the bonds in these cases. In other words it is suggested that the large electron-pair repulsions in the valence-shell of the fluorine atom compared with the other halogens causes the contribution of structures such as (III)



III

to be considerably more important in the fluorides than in the other halides.

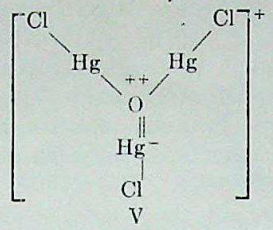
In OX_2^i and NX_3^i molecules, where X^i is a ligand having an incomplete valence-shell, delocalization of the lone-pair electrons on O or N occurs giving partial double-bond character to the OX^i and NX^i bonds which, together with the partial removal of the lone-pair electrons from the central O or N, causes a considerable increase in the bond angles in these molecules. Thus the SiOSi bond angle generally falls in the range 130–140° (Table 7) while the $N(SiH_3)_3$ molecule is planar with 120° bond angles (*20*). In SX_2^i molecules, however, because both S and the ligand X have incomplete valence-shells, there is little tendency for the lone-pairs on S to be transferred to the ligand X^i; and hence the bond angles are less rather than larger than tetrahedral as in the corresponding oxygen compounds. When the ligand X^i in an OX_2^i molecule is a very strong acceptor, e.g., if it is a transition metal, the transfer of the lone-pairs from the oxygen into the OX^i bonds may be essentially complete in which case a linear molecule results (IV). Collinear X^iOX^i bonds have been found in the molecules



IV

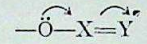
$[Cl_5RuORuCl_5]^{4-}$ and $[TiCl_2(C_5H_5)]_2O$ (*21*, *22*).

Similar delocalization of the oxygen lone-pair electrons occurs in the ion $O(HgCl)_3^+$ which has a plane triangular shape (*23*). We conclude that there must be complete transfer of the oxygen lone-pair electrons into the OHg bonds, i.e., the most important resonance structures are three structures such as (V).

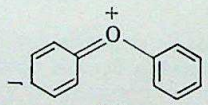


V

Similar effects are observed when the ligand X, although having a complete shell, is unsaturated, i.e., is forming one or more multiple bonds to other atoms, e.g.,



In such a case X behaves as if it had an incomplete shell since one of the electron-pairs of the X=Y double-bond may be partially transferred to Y leaving X electron-deficient and thus facilitating the transfer of lone-pairs on O into the O—X bond. Hence, for aliphatic compounds the COC bond angle is always very close to and generally a few degrees smaller than the tetrahedral angle, but for aromatic compounds the COC angle is generally in the range 120–125° (Table 8). This may be attributed to the partial double-bond character of the O—C bonds, i.e., to the importance of contributing structures such as (VI).



VI

The planar 120° arrangement of the bonds around nitrogen in urea and formamide (*24*, *25*) can also be similarly explained.

The large SOS bond angle found in many molecules may also be accounted for in the same way (Table 9).

Table 7. Si—O—Si and Si—S—Si Bond Angles (in degrees)

Si—O—Si		Si—S—Si	
α-Quartz	142	$(SiS_2)_n$	80
α-Cristobalite	150	$[(CH_3)_2SiS]_2$	75
$(SiO_3^{2-})_n$	137.5	$[(CH_3)_2SiS]_3$	110
$(Cl_3Si)_2O$	130		
$[(CH_3)_3Si]_2O$	137		
$[(CH_3)_2SiO]_3$	136		
$[(CH_3)_2SiO]_4$	142		

Table 8. C—O—C Bond Angles (in degrees)

Aliphatic		Aromatic	
$(C_2H_5)_2O$	108	$(p\text{-}IC_6H_4)_2O$	123
$(CH_3)_2O$	110	$(p\text{-}BrC_6H_4)_2O$	123
1:4 Dioxan	108	$(C_6H_5)_2O$	124
Paraldehyde	109.5	$p\text{-}C_6H_4(OCH_3)_2$	121

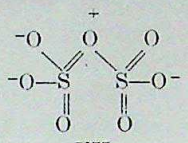
Table 9. SOS, SSS, POP, and PSP Angles (in degrees)

S—O—S		S—S—S	
$(SO_3)_3$	114	S_8	105
$(SO_3)_n$	121	S_n	100
$HS_2O_7^-$	114	S_4^{2-}	104.5
$S_3O_{10}^{2-}$	122	$(C_6H_4SO_2)_2S$	106.5
$S_2O_7^{2-}$	124	$(CH_3SO_2S)_2$	104
		$S_4O_6^{2-}$	103
		$S_5O_6^{2-}$	106
P—O—P		**P—S—P**	
P_4O_6	127.5	P_4S_{10}	109.5
P_4O_{10}	123.5	P_4S_3	102
$P_4O_{12}^{4-}$	132	P_4S_5	107
$(PO_3)_n^{n-}$	129	P_4S_7	106
$P_2O_7^{4-}$	134	$P_4S_3I_2$	104
$P_3O_{10}^{5-}$	122		

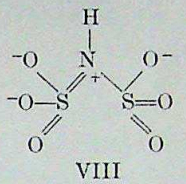
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The S atoms in these molecules have filled valence-shells of six electron-pairs but they are unsaturated in the sense that they are double-bonded to one or more oxygen atoms. Hence, resonance structures such as (VII) make an important contribution to the actual structure. The bond angle in the imino-disulfonate ion $NH(SO_3)_2^{2-}$ has a similarly large value of 125.5° (*26*) due to the important contribution of structures such as (VIII.)



VII



VIII

It is interesting to note that in a molecule in which sulfur has a complete valence-shell of six electron-pairs and does not have any double bonds, e.g., in F_5SOOSF_5 the S—O—O bond angle is only 105° (*27*). The numerous phosphorous compounds in which the POP angle is in the range of 120–130° have P atoms with only four or five electron-pairs and therefore incompletely filled shells. They are also unsaturated because of double-bonds to oxygen atoms. However, S—S—S and P—S—P bond angles are, as expected, generally smaller than 109° (Table 9).

(6) **In a valency shell containing a number of electron pairs, such as five or seven, in which all the electron pairs cannot have the same number of nearest neighbors, then those electron pairs with the greatest number of nearest neighbors will be at a greater average distance from the nucleus than the other electron-pairs.** In AX_2, AX_3, AX_4, and AX_6 molecules symmetry requires all the bond lengths to be identical but in AX_5 molecules the axial and equatorial bonds are not required by symmetry to be the same. The axial electron-pairs have three neighboring pairs at an angle of 90°, while the equatorial pairs have only two neighboring electron-pairs at 90° and two more at 120°. Since the interaction between two electron-pairs at 120° is much smaller than that between two pairs at 90° it is clear that one would not have an equilibrium situation since the total repulsive force on the axial pairs would be greater than on the equatorial pairs. An equilibrium situation is only obtained if the axial pairs are at a greater distance from the nucleus than the equatorial pairs, thus reducing the axial-equatorial interactions. Hence, the axial bonds would be expected to be longer than the equatorial bonds. This conclusion would also be expected to be valid for AX_4E and AX_3E_2 molecules. Indeed, the greater repulsion exerted by the lone-pairs should increase the difference between the equatorial and axial bond lengths. As the data in Table 10 show the axial bonds are indeed longer than the equatorial bonds in all AX_5, AX_4E, and AX_3E_2 molecules for which accurate data are available. Even when the ligands in the axial and equatorial positions are different, subtraction of the covalent radii of the ligand atoms from the observed bond lengths shows that, as expected, the covalent radius of the central atom is greater in the axial than in the equatorial directions (Table 11).

Table 10. Bond Lengths in AX_5, AX_4E, and AX_3E_2 Molecules (Å).

	Axial	Equatorial
PCl_5	2.19	2.04
$SbCl_5$	2.43	2.31
SF_4	1.646	1.545
ClF_3	1.698	1.598
BrF_3	1.810	1.721

Table 11. Equatorial and Axial Radii of the Central Atom in AX_5, AX_4E, and AX_3E_2 Molecules with Different Axial and Equatorial Ligands (Å).

	r_{ax}	r_{eq}
PCl_2F_3	1.06	0.95
$(C_6H_5)_2SeBr_2$	1.36	1.14
$(C_6H_5)_2SeCl_2$	1.31	1.14
$(CH_3C_6H_4)_2SeCl_2$	1.40	1.17
$(CH_3 \cdot C_6H_4)_2SeBr_2$	1.40	1.17
$(CH_3)_2TeCl_2$	1.52	1.33
$(C_6H_5)_2TeBr_2$	1.54	1.37
$IO_2F_2^-$	1.36	1.27
$C_6H_5ICl_2$	1.46	1.23

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The Flash of Genius, 17

The Discovery of the Transistor: W. Shockley, J. Bardeen and W. Brattain

The transistor is one of the most revolutionizing developments in modern electronics. The transistor and its twin, the Bell solar battery, are by-products of fundamental research on semiconductors in the field of solid state physics. Our present knowledge of atomic bonds in metals as compared to covalent bonds in nonmetals and other information about the solid state now makes it possible to understand the clever application of electron theory in developing the transistor.

The procedure for building a transistor or a solar battery now seems to be very simple in terms of the modern theory of chemical bonding. Into a covalent lattice-work place an element whose atoms have five valence electrons. Since this is one more than can be used for bonding, the extra electron behaves as one in a metallic conductor. Into another lattice-work place an element whose atoms have only three valence electrons. This leaves a *hole* into which the extra electrons from the other electrode can move.

The transistor was developed in 1948 by the team effort of American physicists, William Shockley, John Bardeen, and Walter Brattain of the Bell Telephone Laboratories. Dr. Bardeen summarizes the discovery this way:

"As you will note, a solid state amplifier was a long range objective of the research program and was one reason that a study of semiconductors was chosen as a fertile field for research. In fact, Shockley has some ideas on how a solid state amplifier could be made. The research program, however, was a basic research program not directed toward any particular device but toward gaining a deeper understanding of electronic processes in semiconductors. The discovery of the transistor effect was an outgrowth of this basic research program and was in part an accidental discovery. The mode of operation is one which was not anticipated at the start of the program."

He described his work in more detail in his Nobel lecture (*2*). The story of this discovery is related by the Bell Telephone Laboratories in their publication, "The Story of the Transistor" (*3*).

"Early in 1940, Dr. Marvin J. Kelly, then Director of Research for Bell Telephone Laboratories, called into his office several members of his staff who had begun some work on semiconductors. They included Walter H. Brattain, a young physicist. The purpose of the meeting was to watch a demonstration by Russell S. Ohl, a member of the staff who was then studying silicon. Ohl showed his fellow scientists a "little chunk of black stuff," silicon, to which were attached wires leading to a voltmeter. He aimed a flashlight at the silicon, and the meter registered a voltage across the wires. The silicon had converted light into electrical energy as any photoelectric cell might do. There were important differences. . . .

"In January, 1946, active work was resumed, this time under the joint supervision of William Shockley and S. O. Morgan. Brattain, an experimental physicist, conducted the laboratory work on surface properties of semiconductors. . . .

"Shockley predicted that it should be possible to control the movable electrons inside a semiconductor by influencing them with an electric field imposed from outside and without contacting the material. But the results of various laboratory experiments, including those based on Shockley's prediction, disagreed with known theory of how electricity flows across the surface of a semiconductor. The need for a better theory was solved by Bardeen. He believed that electrons are trapped in the surface layers of semiconductors such as germanium and silicon. This concept, the "surface state theory," led to the idea of one sign of charge in the surface traps and an equal and opposite space charge extending into the semiconductor. In other words, a "space-charge layer" may exist at the free surface of a semiconductor, independent of a metal contact.

"Bardeen's theory opened up ways of investigating the electronic behavior at the surface. The next steps were verification and measurement. At Bardeen's suggestion, the semiconductor material was then switched from silicon to germanium. Bardeen and Brattain worked together on the experiments and the arrangement speeded interpretation and discussion and enabled the ideas of both men to be tried with a minimum of delay.

"In his laboratory notes in mid-December, 1947, Brattain recorded observing for the first time what has come to be known as the "transistor effect." From their experiments, Brattain and Bardeen invented the semiconductor amplifier. . . .

"A member of the Bell Laboratories staff, J. R. Pierce, contributed the name for the semiconductor amplifier. He called it a "transistor," from one of its important properties, transfer resistance.

"On June 22, 1948, the point contact transistor—the invention of Bardeen and Brattain—was demonstrated to the technical staff of Bell Laboratories."

Brattain describes some of the early work (*4*):

"In 1874, there came the discovery of rectification at contacts between metals and semiconductors like galena, by F. Braun, whom many of the old-timer "cats's whisker" boys probably remember, and A. Schuster, who noted a similar effect between copper oxide and copper. . . .

"A man by the name of Ohl, a man of some genius, decided to investigate various cat's-whisker materials.

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He got metallurgists at the Bell Telephone Laboratories to try to make uniform silicon ingots, and as a result of this work two things happened.

"The first was that a piece of silicon was made in which one end was *p*-type and the other was *n*-type; the middle was thus a *p-n* junction. The most phenomenal properties were observed. The photo-emf which could be obtained was of an order of magnitude greater than anything which had ever been observed before, even when the light was shining on the edge on the junction and not on the front surface.

"Secondly, the metallurgists Scaff and Theuerer, being good chemists, were aware that they had a detecting mechansim which was even better than spectrographic methods—their noses. The smell of the ingots as they came out of the furnace suggested to them that phosphorus was one of the important impurities, and this indicated the importance of Group III and Group V impurities.

"That was the background, and that was what was available to us when we started as a group after the war to try to see whether we could understand in a physical sense what was going on in these materials. . . .

"My colleague, William Shockley, came up with the thought that if the Mott-Schottky idea of a semiconductor rectifier was right, that it was the contact-potential field which formed the space-charge layer, then an applied field should be able to form such a space-charge layer and from this effect one should be able to change the conductivity in a semiconductor and make an amplifier, in principle. The only trouble was that at first it did not work. . . .

"My colleague, John Bardeen, finally came along with the idea that after all it was naive to assume that the free surface of a semiconductor should be neutral, that the essential concept was that there was a charge on the surface and that the interior of the semiconductor had to be in equilibrium with the surface, and that there should be a space charge at the surface before one ever made contact to it, and that the surface charge layer could shield the interior of the semiconductor from any external field.

"The result was that, through attempts to try to measure the space-charge layer in the semiconductor and a certain ignorance on my part as to the difference between dielectric liquids and electrolytic liquids, we were inadvertently turned to the problem of Becquerel. We found some of the interesting phenomena which occur when one makes the electrolytic contact to germanium or silicon. With a suggestion for optimum geometry by John Bardeen, we were able to make the field effect work. In trying to get rid of the electrolyte and in trying to make a field-effect amplifier without an electrolyte, we inadvertently made a good emitter contact to germanium, and on investigating the properties around that contact, we discovered the transistor effect."

In a later paper (*5*) Brattain concludes:

"As far as I am concerned the advent of the transistor is one of those developments that come along when general background knowledge has developed to such a stage that human minds are prepared to take a new step in the understanding of phenomena that have been under observation for a long time. . . .

"The picture of a *semiconductor as a medium in which electrons and holes, as dissociated covalent bonds, can exist in thermodynamic equilibrium* was the necessary conceptual idea. It is closely analogous to the quantum mechanical concept of electrons and positrons in vacuum. Another close analogy is to the theory of dissociation in electrolytes."

Shockley adds this in his Nobel address (*6*):

"The experiment which played the largest role in stimulating the transistor electronics program at Bell Telephone Laboratories was the so-called field-effect experiment. I devised this experiment as a direct result of trying to invent a semiconductor amplifier having separate input and output circuits. From the then known properties of semiconductors, I concluded that a thin film of silicon or germanium would have a substantial change in its conductivity if it were made into one of a pair of condenser plates and the condenser strongly charged. The surface charge, if represented as a change in mobile carriers could appreciably increase or decrease the conductance of the film.

"A number of experiments were initially tried using evaporated layers and other thin layers. These all gave negligible effects and progress was at a standstill until Bardeen proposed his theory of surface states to explain the lack of an observable effect.

"Bardeen's model also explained a number of other previously mysterious phenomena and led to the suggestion of doing the field-effect experiment at liquid air temperature to immobilize the surface states. This gave the first positive result."

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Editor's Note

This is the final installment of the "Flash of Genius" series. One or more items has appeared each month in THIS JOURNAL since June 1962. These 17 along with 34 other stories of discovery by the discoverers themselves are contained in Prof. Garrett's book "Flash of Genius" published May 17 by D. Van Nostrand Company, Inc., Princeton, N. J. The book contains 260 pages and is priced at approximately $6.50.

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Stable Gaseous Species at High Temperatures

If one heats gases which have relatively strong bonds to sufficiently high temperatures that appreciable bond rupture occurs, the dissociation profile at such a temperature from a gas of the type MX_n will depend upon the relative bond strengths in the dissociated species, MX_{n-1}, MX_{n-2} - - - MX. From a consideration of the dissociation energies for such a sequence of reactions, it is possible to predict the major species that will be stable at very high temperatures. Such a procedure is pedagogically important because it can lead to an intuitive prediction of the species that are stable at high temperatures. In addition, the reasons for the variations in bond strengths in dissociation sequences are informative in themselves in terms of the nature of chemical bonds. A number of such dissociation sequences will be analyzed from this point of view in this paper. Since fluoride and oxide gaseous species are often stable at quite elevated temperatures and the bonding principles for these dissociative sequences are particularly interesting, each of these types will be discussed in turn.

Some diatomic and polyatomic elemental gases are of course also stable to high temperatures, although many are not. A systematic correlation of the bonding in the gaseous molecules of the elements with the strengths of their respective bonds is also presented in this paper.

Fluoride Sequences

Beryllium fluoride, BeF_2, has been described previously in terms of the intrinsic bond energy concept (*1*) and need not be repeated here. Consideration of the dissociation products from BF_3 are quite interesting; the energetics are given below.[1]

Bond energy, E (kcal/mole)	Sequence	Dissociation energy, ΔH (kcal/mole)
~153	$BF_3 \rightarrow BF_2 + F$	~153
~153	$BF_2 \rightarrow BF + F$	~108
~198	$BF \rightarrow B(g) + F$	~198

From these data it is evident that the boron-fluorine bond in the BF molecule is considerably stronger than in BF_3 or BF_2. Because the dissociation energy for the dissociation of BF_2 is much less than that for BF_3 or BF, it can be predicted that if sufficient energy is present to dissociate BF_3, then BF_2 will also dissociate to BF + F. Accordingly it is BF rather than BF_2 that should be the high temperature stable species.[2] Note that the high dissociation energy for BF precludes significant dissociation to $B(g)$ at moderately high temperatures. BF can, of course, be converted to the atoms at even higher temperatures; at atmospheric pressure BF is barely dissociated at 4000°K and decomposes drastically only at temperatures greater than 5000°K.[2]

The greater bond energy for BF as compared to BF_2 and BF_3 is attributable to the greater tendency of the BF molecule to form a partial double bond. Since the sigma bond in BF is undoubtedly mainly a *p-p* bond, lone pair electrons of the fluorine atom can overlap with either of two empty pi orbitals of the boron atom. On the other hand this tendency is very much reduced in BF_3 and BF_2 in which the boron atoms are hybridized and only single empty pi orbitals are present. Also the ionic character of the bond in BF should be greater than that of individual bonds in BF_2 and BF_3 which must distribute ionic character among their several bonds.

The dissociation pattern for $AlF_3(g)$ is qualitatively similar to that for BF_3, with bond energies of ~140 and ~158 kcal/mole for AlF_3 and AlF, respectively. Note the considerably weaker bond in AlF as compared to BF. This is attributable to a lesser tendency for second period elements, such as aluminum, toward multiple bond formation.

The energetics of the CF_4 sequence are as follows.

Bond energy, E (kcal/mole)	Sequence	Dissociation energy, ΔH (kcal/mole)
116	$CF_4 \rightarrow CF_3 + F$	(107)
(119)	$CF_3 \rightarrow CF_2 + F$	(103)
~127	$CF_2 \rightarrow CF + F$	~139
115	$CF \rightarrow C(g) + F$	115

The quantities in parentheses are based on an estimated value forthe heat of formation of CF_3. Since this value has not been determined experimentally, these data are tentative.

On the basis of the dissociation energies one can predict that CF_2 and CF_3 would be more prevalent at high temperatures than would CF, with increasing temperatures favoring CF_2 over CF_3. This is in fact the case. Moreover because of the considerably lower dissociation energy for the CF molecule, as compared to BF, it can be predicted that dissociation to the atoms will occur at much lower temperatures for CF; this is also observed.

The bond energy pattern for CF_4, CF_3, and CF_2 are explained simply on the basis of increasing bond strength for comparable sp^3, sp^2, and sp bonds; this generally follows the order of the magnitude of the overlap integral for such bonds, $sp > sp^2 > sp^3$, with a

[1] Unless otherwise stated the energy terms in this paper were computed from thermochemical data in the "JANAF Thermochemical Tables," Dow Chemical Company, Midland, Mich., 1961. The energy values are given in kcal/mole at 25°C. The bond energy term E is for the undissociated species for each sequence and is simply the atomic heat of formation divided by the number of bonds; ΔH is the dissociation energy for the reaction.

[2] Confirmatory high temperature dissociation data for this sequence and for most of the following sequences can be found in SIEGEL, B., AND SCHIELER, L., "Principles of Propellants," John Wiley, New York, in press.

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greater increment for sp over sp^2.[3] However, if the CF molecule were simply bonded by p-p bonding, as is the case for the CH molecule, then the bond energy for CF would be considerably less than for the bonds in CF_4. Since this is not the case it must be assumed that the increased strength of the bond in diatomic CF results from partial double bonding, of the type already discussed for BF. Note that for CF_2, CF_3, and CF_4 there are no empty pi orbitals on the carbon atom, but there is an empty pi orbital for the ground state CF molecule prior to pi bonding.

The bond energies for SiF_4 and SiF are ~140 and 119±12 kcal/mole. Note that unlike the CF_4 and CF case, there is a substantial drop in bond energy between the higher and lower fluoride; in the case of Si, once again there is no extra stabilization of the diatomic fluoride due to partial double bonding. The increase in bond energy for the bonds in SiF_4 over those in CF_4 reflect the weaker bonds formed by the fluorides of electronegative elements, since C is considerably more electronegative than Si. The fluoride bonds of N and O are weaker still and are not stable at high temperatures. Since phosphorus is less electronegative than nitrogen, the phosphorus-fluorine bonds are stronger than N-F bonds. The bond energies for PF_3 and PF are ~115 and ~113 kcal/mole, respectively; and one can obtain a rough estimate of 112 kcal/mole for PF_2. Accordingly each of these phosphorus fluoride species is a probable high temperature specie. The bonding in ClF_3 is too weak for this interhalogen molecule to be stable at elevated temperatures; similarly the dissociation energy for the simplest species ClF is ~62 kcal/mole and this molecule is also thermally labile.

Oxide Sequences

The lightest oxide is H_2O, for which the dissociation energetics are as follows

Bond energy, E (kcal/mole)	Sequence	Dissociation energy, ΔH (kcal/mole)
110.5	$H_2O \rightarrow OH + H$	119
102	$OH \rightarrow O + H$	102

Since the dissociation energy for OH to the atoms is less than that for the first step, it is predictable that the dissociation of water will lead to greater quantities of the elements O and H than simply OH. At atmospheric pressure water decomposes drastically at temperatures above 2000°K and is virtually decomposed at equilibrium at 4000°K. However, at temperatures below 3000°K the elements are mainly in the molecular form of H_2 and O_2. Above this temperature the latter becomes increasingly dissociated to H and O.

The difference in bond energy for the bonds in H_2O and OH can be explained on the basis of two separate models. We can first consider the model in which both H_2O and OH are essentially unhybridized. The oxygen atom in OH must be promoted from the ground state atom to the simple valence state, which involves an uncoupling energy for the two unpaired electrons of the ground state oxygen atom. Upon dissociation of H_2O to OH + H, one does not obtain the ground state oxygen atom. However, upon dissociation of OH to H + O, the ground state oxygen atom is formed, releasing the uncoupling energy described above. This energy release is exothermic and reduces the dissociation energy beyond the value for dissociation of OH to the valence states of the atoms (*1*). For this reason the bond energy for H_2O should be greater than for OH. The second model for H_2O considers this molecule to be sp^3 hybridized, with extra p character, to explain the deviation of the valence angle from the tetrahedral angle. If OH is essentially unhybridized while H_2O is hybridized, one would expect stronger bonding in the H_2O molecule because hybrid bonds are stronger than unhybridized bonds of the same type.

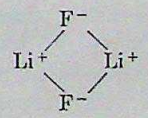
Compared to HF which has a dissociation energy of 135 kcal/mole, the water sequence is more weakly bonded and is thus more drastically dissociated at high temperatures. Unlike H_2O, HF at atmospheric pressure is drastically dissociated only at temperatures above 4000°K.

The gaseous Li_2O molecule has a valence angle of 110° but this angle does not indicate whether the molecule is ionic or covalent since both models are predicted to be bent (*2*). The bond energies for bonds in Li_2O and LiO are ~85 and ~84 kcal/mole, with dissociation energies of ~86 and ~84 kcal/mole for the reactions

$$Li_2O \rightarrow LiO + Li, \text{ and } LiO \rightarrow Li + O$$

On this basis Li_2O will dissociate at temperatures considerably below those characteristic of H_2O. Unlike the H_2O sequence the bond energies in Li_2O and LiO are almost identical, within an uncertainty of several kcal/mole. One can thus infer that considerably less hybridization is characteristic of the Li_2O molecule, and that Li_2O is more ionic than H_2O; this is consistent with the weaker electronegativity of lithium as compared to hydrogen.

Lithium fluoride is bonded more strongly than is Li_2O. The vapor of lithium fluoride at temperatures below 2000°K does not consist of LiF(g) alone, but also of polymers of the type $(LiF)_2$ and $(LiF)_3$. Not only is LiF(g) ionic but the polymers are also probably ionic with planar structures such as (*3*).



The energetics are as follows

Sequence	Dissociation energy, ΔH (kcal/mole)
$(LiF)_3 \rightarrow (LiF)_2 + LiF$	~ 43
$(LiF)_2 \rightarrow 2\ LiF$	~ 64
$LiF \rightarrow Li(g) + F$	~137

From these data it is evident that $(LiF)_n$ species will not be important at temperatures above 2000°K. Because of its strong bond, LiF does not significantly dissociate below 3500°K, at atmospheric pressure.

Crystalline beryllium oxide has the high value of 174 kcal/mole for the sublimation energy to BeO(g), with

[3] For a discussion and table of overlap integrals, see MULLIKAN, R. S., ET AL., *J. Chem. Phys.*, 17, 1248 (1949); MULLIKAN, R. S., *J. Am. Chem. Soc.*, 72, 4493 (1950); MULLIKAN, R. S., *J. Chem. Phys.*, 19, 900 (1951). The difluoride is considered to be linearly hybridized by analogy to the CH_2 molecule which has been shown to be linear: ANET, F. A. L., ET AL., *J. Am. Chem. Soc.*, 82, 3217 (1960); FREY, H. M., *J. Am. Chem. Soc.*, 82, 5947 (1960).

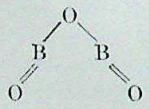
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an estimated normal boiling point of ~4100°K. Since the dissociation energy for $BeO(g)$ to the atoms is only ~108 kcal/mole, one should not expect the vapor over $BeO(s)$ at the boiling point to contain much gaseous oxide; this is in fact the case. That the vapor contains even moderate amounts of oxide at the boiling point is attributable to the fact that $BeO(s)$ can decompose to polymeric gaseous oxides, a step requiring less energy than complete decomposition to $BeO(g)$. Thus at ~4100°K the vapor consists of Be_3O_3 and Be_2O_2, as well as BeO, and the atoms Be and O; at 5000°K, virtually complete dissociation to the atoms occurs at equilibrium. The polymeric gaseous beryllium oxides have been observed mass spectrometrically and they have been assigned ring structures as the probable configurations (*4*).

Magnesium oxide is similar to $BeO(s)$ in that the sublimation energy is high (~148 kcal/mole) by comparison with the dissociation energy for $MgO(g)$ (~91 kcal/mole). Accordingly the vapor above the boiling point is unlikely to contain much oxide. However, unlike $BeO(s)$ magnesium oxide polymers are not observed (*4*).

High temperature mass spectrometric studies of the vapor over $B_2O_3(s)$ indicate that $B_2O_3(g)$ decomposes to $BO(g)$ and oxygen. However, the probable structure of $B_2O_3(g)$ is (*5*)



and dissociation of this molecule should produce BO + BO_2 in a primary step. Although BO_2 has not been observed mass spectrometrically there is infra-red spectral evidence for its formation (*6*). Since the energy required to dissociate $B_2O_3(g)$ to 2BO+O is ~278 kcal/mole and rupture of the O-B bond of $B_2O_3(g)$ should be roughly equivalent to that for $BO_2 \rightarrow$ BO + O, one can estimate a dissociation energy of approximately 139 kcal/mole for the latter step. This should make BO_2 stable to reasonably high temperatures.

Considerably more energy is required to dissociate the BO molecule because of its multiple bonding. The high value of 186 kcal/mole for this energy step indicates that the bond in BO is higher than simply a double bond and the latter may have partial triple bond character. At very high temperatures BO is the most stable boron oxide species and is largely undissociated at 6000°K. At temperatures below 5000°K significant association of BO to O=B-B=O occurs, but the boron-boron single bond in the latter is obviously weaker than the boron-oxygen linkages.

High temperature mass spectrometric studies of the vapor over $Al_2O_3(s)$ under neutral conditions indicate that AlO, Al_2O, and Al_2O_2 are formed but $Al_2O_3(g)$ was not observed; however, it has been reported that vapor pressure data for this system at 2300–2600°K indicate that $Al_2O_3(g)$ is present (*7*). It is evident that the structure of $Al_2O_3(g)$ must be quite different from that of $B_2O_3(g)$, which is observed to be a major species over $B_2O_3(s)$. This is also indicated by the presence of Al_2O and the absence of B_2O. That the two structures are different should be expected since second period elements such as aluminum form weaker double bonds than do first period elements such as boron. This is strikingly demonstrated by the relative dissociation energies for BO and AlO. While BO requires ~186 kcal/mole for dissociation, AlO requires only ~116 kcal/mole. Thus while BO is stable to very high temperatures, AlO is not; and it can be predicted that $Al_2O_3(g)$ would be largely dissociated to the atoms at 5000°K.

Another striking example of the difference in bonding between first and second period oxides is given by the following data.

Bond energy, E (kcal/mole)	Sequence	Dissociation energy, ΔH (kcal/mole)
192	$CO_2 \rightarrow CO + O$	127
257	$CO \rightarrow C(g) + O$	257
151.5 ± 12	$SiO_2(g) \rightarrow SiO + O$	~112
191 ± 12	$SiO \rightarrow Si(g) + O$	191 ± 12

Note that the bond energies for the double and triple bonds in CO_2 and CO are considerably greater than for the comparable bonds in SiO_2 and SiO. Both CO and SiO have such high values for their dissociation energies that these species are stable to very high temperatures, although CO_2 and SiO_2 are stable to only moderately high temperatures. At atmospheric pressure CO_2 is more than half dissociated to CO at temperatures above 3100°K and is virtually completely converted to CO at 4000°K.

Whereas the NF compounds are weakly bonded and are thermally labile at elevated temperatures, the possibility of forming multiple bonds for the nitrogen oxides leads to stronger bonds for these molecules. The bond energies are 112 and 151 kcal/mole for NO_2 and NO, respectively. Thus there is a rather low dissociation energy of ~73 kcal/mole for $NO_2 \rightarrow$ NO + O, which makes NO considerably more stable than NO_2 at high temperatures. In the molecular orbital approach to bonding, NO is considered to have a bond order intermediate between a double and triple bond, with a single electron in an antibonding molecular orbital partially canceling one of three filled bonding orbitals. The corresponding phosphorus oxide, PO, has a dissociation energy of ~141 kcal/mole, somewhat less than that for nitric oxide; however the value for PO is sufficiently high that this molecule is stable to high temperatures.

Dissociation Energies of Diatomic Molecules of the Elements

Molecule	Dissociation energy, kcal/mole at 25°C
Li_2	26.4 ± 1.7
Be_2	...
B_2	66 ± 19
C_2	143 ± 3
N_2	226 ± 2
O_2	119.2
F_2	37.8 ± .4
Na_2	19
Mg_2	...
Al_2	...
Si_2	83 ± 34
P_2	117 ± .5
S_2	100.6 ± 1.5
Cl_2	58 ± 4

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Lithium. Dissociation energies in kcal/mole at 25°C are given in the table for the dissociation of the diatomic homopolar gas molecules of the elements.[1] It is seen that the value for Li_2 is quite small. The weak bonding in the Li_2 molecule is characteristic of the alkali metal molecules of this type and is attributable to the small orbital overlap for the 2 *s* electrons of these atoms. As the electronegativity of the alkali metal decreases the bonds in the corresponding diatomic elemental molecules become progressively weaker. Thus the dissociation energies at 0°K for the series Li_2, Na_2, K_2, Rb_2, and Cs_2 fall from 25 to 10.4 kcal/mole (*8*). From these data it is obvious that the diatomic elemental gases of the alkali metals are not stable at elevated temperatures.

Boron. From the table it can be seen that B_2 also has a greater dissociation energy than Li_2. Since boron has the s^2p electronic configuration in the ground state of the atom, it is not necessary for this atom to hybridize in B_2 formation and the molecule has essentially an unhybridized bond. It is difficult to evaluate the probable stability of B_2 from the dissociation energy data because of the large uncertainty in these data. However, it is known that at its boiling point boron vapor is largely monatomic (*9*).

Carbon. Unlike boron, carbon is able to form a double bond in C_2 without the necessity for hybridization. This is verified by the $^1\Sigma$ ground spectroscopic state for C_2 (*10*), which indicates that there are no unpaired electrons in this molecule. The double bond in C_2 leads to the high dissociation energy given in the table. In addition to a diatomic homopolar molecule, carbon also forms chains in the gaseous phase. The dissociation energy for the C_3 molecule to $C_2 + C(g)$ is 180 ±4 kcal/mole. This high value indicates that both bonds in C_3 are multiple bonds. The spectroscopic multiplicity of C_3, in the ground state is 1 (*11*), so that this molecule also has no unpaired electrons. This structure corresponds to an *sp* hybrid configuration for the central carbon atom and double bonds to each of the terminal carbon atoms, the latter being unhybridized.

In any event the high dissociation energies for C_2 and C_3 indicate that these species are stable to very high temperatures.

Nitrogen. The bonding in N_2 is even more stable then that of C_2 or C_3 because the nitrogen atoms in N_2 form a triple bond; note that hybridization is not required in N_2 because each N atom has single electrons in three pi orbitals. At atmospheric pressure N_2 is less than ten percent decomposed at equilibrium at 5500°K, and is barely dissociated at this temperature at a pressure of 50 atmospheres.[2]

Oxygen. The dissociation energy to the atoms is considerably smaller for O_2 as compared to N_2 because O_2 has only a double bond. Accordingly O_2 decomposes at lower temperatures and is significantly dissociated at atmospheric pressure in the range 3000 to 4000°K.

Oxygen also forms the gaseous O_3 molecule, which is a bent molecule with equivalent bond distances of 1.278 Å (*12*). The latter is longer than the 1.208 Å characteristic of O_2 and thus the bonds in ozone are intermediate between single and double bonds,



However the chain bonds in O_3 are considerably weaker than for C_3. Dissociation of O_3 to $O_2 + O$ requires only 26 kcal/mole at 25°C.

Fluorine. Among first period elements the bonding in fluorine is stronger only than that characteristic of Li_2. The weak bonding in F_2 is attributable to the repulsive effect of the three lone pairs of electrons on the single bond. This effect is reduced for the larger chlorine atoms and thus Cl_2 has a higher dissociation energy than has F_2, although the bonding is essentially the same type. However, as one goes down group VII in the periodic table, Br_2 and I_2 become progressively weaker in bonding than Cl_2 (the dissociation energies at 0°K for Br_2 and I_2 are 45.5 and 35.6 kcal/mole) (*8*).

Silicon. Despite the rather large uncertainty in the dissociation data for Si_2, it is clear that Si_2 is more weakly bonded than is C_2. Based on an estimated value for the dissociation energy of Si_3 to $Si_2 + Si$ of 101 kcal/mole (*13*), this molecule is also more weakly bonded than is C_3. This trend of lower dissociation energies is maintained as one goes down the group IV elements. Thus the dissociation energies at 0°K for Ge_2, Sn_2, and Pb_2 are 65, 46, and 23 kcal/mole (*8*). This further verifies that multiple bonding is less prevalent for the higher period elements than for carbon.

Phosphorus. Diatomic phosphorus has a dissociation energy of only approximately half that of N_2. Yet P_2 has the ground spectroscopic state of $^1\Sigma$ and thus has no unpaired electrons. While formally one must therefore consider P_2 to be triply bonded, it is obvious that the triple bond in this molecule is considerably weaker than that in N_2. Phosphorus has also been observed to form the P_4 molecule. The latter is tetrahedral with P-P bond distances of 2.21 Å, as compared to 1.894 Å in P_2. This certainly indicates that the bonds in P_4 are single bonds, and the dissociation data support this conclusion since the reaction $P_4 \rightarrow 2P_2$ requires only 55 kcal/mole.

As was shown to be the case for the group IV elements, the heavier group V diatomic molecules have weaker bonds than N_2 or P_2, the dissociation energies at 0°K falling from 91 to 39 kcal/mole from As_2 to Bi_2. (*8*).

Sulfur. S_2 has a ground state configuration similar to that of O_2, in that it is a diradical (*10*). Nevertheless, the bond in S_2 is weaker by some 19 kcal/mole. Sulfur also forms the octatomic molecule S_8. Dissociation of S_8 to $4S_2$ requires 99 kcal/mole at 25°C. The structure of S_8 is that of a puckered ring (*12*). Cottrell gives 65 and 53 kcal/mole for the dissociation energies of the heavier group VI diatomic molecules Se_2 and Te_2.

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Relationship of Exothermicities of Compounds to Chemical Bonding

The sign and magnitude of the standard heat of formation of a chemical compound is often used incorrectly to characterize its relative stability compared to other compounds. Compounds with large negative heats of formation are often loosely considered more stable than those with smaller negative heats of formation or especially those with positive heats of formation. While in fact such a rule is often qualitatively correct in regard to thermal stabilities of compounds, there are many exceptions in which endothermic compounds are more thermally stable than exothermic ones. Clearly an understanding of the relationship between the exothermicity or endothermicity of a chemical compound and its constituent bond strengths is quite important.

It should be recognized that both kinetic and thermodynamic equilibrium processes contribute to the thermal stabilities of compounds. Considering thermodynamic equilibrium first it is clear that the relative exothermicity or endothermicity of a compound cannot be determined on the basis of bond strength alone. Nitric oxide has a positive heat of formation at 25°C and is thus endothermic. Yet the dissociation energy of NO to the atoms is quite high (151 kcal/mole).[1] Compared to F_2, which has a dissociation energy of 38 kcal/mole and which is arbitrarily assigned a zero heat of formation, NO is obviously more strongly bonded despite its relative endothermicity. Similarly N_2 is also arbitrarily assigned a zero heat of formation but is much more strongly bonded than F_2 (dissociation energy of N_2 is 226 kcal/mole).

Kinetics become important in consequence of the magnitude of the activation energy. The latter is obviously related to the strengths of chemical bonds. Thus NO which has a high dissociation energy because of its high bond order obviously requires a high value for the activation energy for dissociation. Despite its endothermicity NO does not decompose appreciably at normal temperatures because sufficient numbers of NO molecules do not possess the required high activation energy; in fact, NO is stable to temperatures exceeding several thousand degrees. On the other hand F_2, which is exothermic relative to NO, is thermally labile at temperatures not much above room temperature because of the low activation energy for dissociation required by the weak F-F linkage.

The purpose of this paper is to discuss an interpretation for the sign and magnitude of the standard heats of formation of chemical compounds. This will be accomplished by analyzing the component energies that contribute to the heats of formation and clarifying the dependence of heats of formation on bond strengths in different types of molecules.

Heat of Formation Cycle

Since the standard heat of formation of a compound is defined as the heat liberated when the compound is formed from the elements in their standard states, the following energy steps contribute to its magnitude.

Heats of atomization of the component elements—endothermic.
Heat of formation of the gaseous compound from the gaseous atoms—exothermic.
Heat of condensation for compounds which are in a condensed state—exothermic.

Using the heat of formation of crystalline BeO(*s*) as an example, the following energy steps must be considered:

$$\mathrm{Be}(s) \rightarrow \mathrm{Be}(g) \quad (1)$$
$$\tfrac{1}{2}\,\mathrm{O}_2 \rightarrow \mathrm{O} \quad (2)$$
$$\mathrm{Be}(g) + \mathrm{O} \rightarrow \mathrm{BeO}(g) \quad (3)$$
$$\mathrm{BeO}(g) \rightarrow \mathrm{BeO}(s) \quad (4)$$

The standard heat of formation of gaseous BeO is the sum of the heats associated with steps 1 through 3, and its sign and magnitude are determined by the extent to which the exothermicity of step 3 overcomes the endothermicity of steps 1 and 2. Step 3 is vigorously exothermic only for the formation of very strong bonds. In the case of BeO(*g*), the beryllium-oxygen bond is reasonably strong, with a dissociation energy to the atoms of 108 kcal/mole. Nevertheless BeO(*g*) is

[1] The thermodynamic data presented in this paper were originally taken or computed from data in the "JANAF Thermochemical Tables," Dow Chemical Company, Midland, Mich., 1961. For simplicity all data are given at 25°C.

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endothermic because the atomization energies for Be(s) and $^1/_2$ O_2 (78.3 and 59.6 kcal/mole, respectively) exceed the magnitude of the dissociation energy for BeO. It is due to the high values for the atomization energies of N_2 and O_2 that NO is also endothermic, despite its strong bonding.

It becomes apparent that diatomic gaseous molecules are generally endothermic because the exothermicities of single bonds often cannot overcome the endothermic effect of the atomization of the elements. Carbon monoxide also demonstrates the validity of this rule since it is barely exothermic ($\Delta H_f°$ is only −26.4 kcal/mole) despite the fact that it has the highest dissociation energy of any diatomic molecule; the latter value of 257 kcal/mole is attributable to the stable triple bond in CO. Strongly exothermic diatomic molecules thus require not only high dissociation energies but low values for the heats of atomization of the elements. For this reason exothermic diatomic molecules are generally the fluorides and chlorides of the less electronegative elements, because such molecules have strong bonds and the heats of atomization of F_2 and Cl_2 are quite low (the heats of formation of F and Cl are 19 and 29 ± 2 kcal/mole, respectively).

Polyatomic molecules are more apt to be exothermic than are diatomic molecules, because the larger number of bonds in polyatomic molecules result in greater exothermicities for step 3. Also, although the number of atoms is increased in polyatomic molecules, the endothermic effect of the atomization energies of the elements is reduced *per bond*. Carbon monoxide and dioxide provide a convenient example.

$$\begin{array}{rr} C(s) \rightarrow C(g) & C(s) \rightarrow C(g) \\ {}^1/_2\ O_2 \rightarrow O & O_2 \rightarrow 2O \\ C(g) + O \rightarrow CO & C(g) + 2O \rightarrow CO_2 \end{array}$$

Whereas the exothermicity of the lone bond in CO is reduced by the atomization energy for C(s) and $^1/_2$ O_2, each bond in CO_2 is affected by $^1/_2$ C(s) and $^1/_2$ O_2. This reduction of the endothermic effect of the heat of atomization of carbon (the heat of atomization of carbon is 171 kcal/mole) makes CO_2 more exothermic than CO despite the weaker carbon-oxygen double bonds in CO_2 compared to the triple bond of CO. For molecules not involving such a change in bond order, the increase in exothermicity with number of bonds is more pronounced; this will be illustrated in the next section.

Returning to the example of BeO(s) it should be noted that BeO(s) is exothermic while BeO(g) is not. The difference stems from the heat of crystallization of BeO(g), step 4 of the heat of formation cycle. In this case there is a huge change in the heats of formation since BeO(s) is strongly exothermic with a heat of formation of −143 kcal/mole. The difference is simply a heat of crystallization of 174 kcal/mole.[2] The magnitude of this energy term strongly affects the degree of exothermicity of crystalline compounds. In general if the gaseous molecule contains a small number of bonds (as in a simple diatomic molecule such as BeO(g)) and the crystalline phase is characterized by a high coordination number, then there will be a large heat of crystallization; if there is only a slight change in the number of bonds upon crystallization then the corresponding energy change will be small. Since there is only a single bond in BeO(g) and BeO(s) has the 4:4 coordinated Wurzite structure, the crystallization energy is very large indeed. As a general rule it can be stated that crystallization increases the exothermicity of exothermic gases and in many cases converts endothermic gases to exothermic solids. The conversion of a gaseous molecule to the liquid phase generally produces a lower order of exothermicity than formation of crystalline phases.

[2] Note that this term is not the lattice energy. The latter is defined as the energy released when a crystalline phase is formed from the gaseous *ions*. The heat of crystallization as used in this paper is the heat liberated when the crystalline phase is formed from the gaseous *molecule*.

Dependence on Bond Strengths

The influence of bond strength on the exothermicities of compounds can be demonstrated conveniently by consideration of the fluorides of the first two rows of the periodic table. Data is presented in Table 1 on the bond energies (heat of formation from the atoms divided by the number of bonds in the molecule), heats of crystallization and standard heats of formation of these fluorides. It is seen that for the strong bonds characteristic of LiF, BeF_2 and BF_3, exothermicity rises almost linearly with the number of bonds for the gaseous molecules; the crystalline solids LiF(s) and BeF_2(s) have disproportionately high exothermicities due to their heats of crystallization. However, for the fluorides of the electronegative elements the bond energies fall rapidly with increasing electronegativity and the heats of formation become increasingly less negative. That this is attributable largely to the difference in bond strengths rather than to the effect of the heats of atomization of the elements is shown by the data for NF_3-BF_3 and OF_2-BeF_2; the heats of atomization of $^1/_2$ N_2 and B(s) are not very different (113 and 132.5 kcal/mole) and those for $^1/_2$ O_2 and Be(s) are also nearly equivalent (59.6 and 78.3 kcal/mole).

The data for second row fluorides are strikingly different than those of the first row fluorides for elements of groups IV through VII. It can be seen that the bond energies are considerably larger for comparable

Table 1. Thermochemical Data for Fluorides of the Light Elements.

Compound	E (kcal/mole)	ΔH_c (kcal/mole)	$\Delta H_f°$ (kcal/mole)
LiF (s)	137 ± 3.5	66 ± 3	−145 (−79 for LiF(g))
BeF_2 (s)	150.5 ± 2.5	57 ± 10	−241 ± 5 (−184.5 for BeF_2(g))
BF_3	153 ± 2	...	−270 ± 2
CF_4	116	...	−218 ± 1
NF_3	67 ± 1	...	− 30 ± 2
OF_2	45 ± 1	...	7.5 ± 2
F_2	19	...	0
NaF (s)	112	69	−136 (−67 for NaF(g))
MgF_2 (s)	125 ± 2	86 ± 7	−262.5 ± 3 (−176.5 for MgF_2(g))
AlF_3 (s)	140 ± 2	71 ± 10	−356 ± 5 (−285 for AlF_3(g))
SiF_4	140 ± 3	...	−373
PF_5	111	...	−381
SF_6	78	...	−288.5
ClF_3	42 ± 1	...	− 39 ± 1

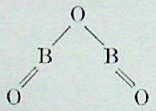
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second row fluorides. This results in increased exothermicities for the latter. The reason for stronger bonds in SiF_4 compared to CF_4, PF_5 compared to NF_3, SF_6 compared to OF_2 and ClF_3 compared to F_2, is the lower electronegativities of the second row elements and their use of partial *d* hybridization to form stronger sigma bonds than the comparable first row elements.

Comparison of oxides and fluorides is informative. Based on bond energies of 86 ± 3 and 108 kcal/mole for the bonds in Li_2O and BeO, the oxides of Li and Be are formed from bonds that are much weaker than the fluorides of these metals. Accordingly while the gaseous fluorides are exothermic, BeO is endothermic and $Li_2O(g)$ is barely exothermic, although the crystalline oxides of these metals are strongly exothermic because of large crystallization energies (174 and 109 kcal/mole). The crystallization energies for these oxides are considerably larger than for the fluorides because formation of strong bonds in the solid phase releases more energy if the gas phase molecules are weakly bound.

Unlike Li_2O and BeO, stronger oxygen bonds are formed with elements that can produce multiple bonds. Thus $B_2O_3(g)$, which has the probable structure[3]



is quite exothermic (ΔH_f° of −210 kcal/mole); the exothermicities of CO_2 and CO were previously discussed. That CF_4 is more exothermic than CO_2 is attributable to the larger number of bonds in the fluoride since the bond energy of the carbon-oxygen double bond in CO_2 (192 kcal/mole) far exceeds the C—F bond energy in CF_4. It is also of interest to compare CO_2 with SiO_2. Each Si—O bond in gaseous SiO_2 has a bond energy of 151.5 ± 6 kcal/mole, a value considerably less than that for the bonds in carbon dioxide. Despite a smaller heat of atomization of silicon (110 ± 12 kcal/mole) as compared to carbon, the lower bond energy for the Si—O bond makes $SiO_2(g)$ barely exothermic, less so than CO_2. That the Si—O bond is weaker than the carbon-oxygen bond in CO_2 is attributable to the fact that second period elements form weaker double bonds than do first period elements. Gaseous SiO_2 crystallizes to $SiO_2(s)$, releasing the large crystallization energy of 136 kcal/mole in forming the tetrahedrally coordinated silica structure; this makes crystalline SiO_2 more exothermic than CO_2.

Dependence on Heats of Atomization of the Elements

This subject has been discussed in several instances in the previous sections for specific compounds. A more general viewpoint can be obtained from the data in Table 2 which presents the atomization energies per bond for the elements of the first row of the periodic table in compounds based on usually encountered maximum valences. From Table 2 it can be seen that for such compounds, the atomization energies per bond become roughly equivalent, although O and F are somewhat lower. This certainly demonstrates the large endothermic effect for compounds based on lower valences and indicates that exothermicity is favored by the formation of higher valence compounds.

A simple example of this rule is the increasing endothermicity of the series of hydrocarbons: ethane, ethylene, and acetylene. Whereas the atomization energy of carbon, per bond, is 48.8 kcal/mole for ethane, it rises to 68.4 for ethylene and to 113.9 for acetylene. Accordingly, acetylene is more endothermic than ethylene, while ethane is exothermic. It should be emphasized that the decreasing exothermicity in this series is not due to chemical bond strengths. On the contrary, the carbon to carbon bonds become increasingly stronger from the single bond in ethane to the triple bond in acetylene. Also the strengths of the C-H bonds increase in the series from ethane to acetylene because sp^3 bonds are weaker than sp^2 bonds which are still weaker than *sp* bonds.[4]

Table 2. Effect on Endothermicity of Atomization Energies of Light Elements.

Element	Valence	Atomization energy per bond (kcal/mole)
Li	I	38.4
Be	II	39.2
B	III	44.2
C	IV	42.7
N	III	37.7
O	II	29.8
F	I	18.9

Effect of Catenated Bonds

Compared to carbon the other elements of the first two rows of the periodic table form relatively weak catenated single bonds. For this reason catenation tends to reduce the exothermicity of compounds in which it occurs. Although rare for elements of the first three groups, the catenated bonds >N—N< and —O—O— are found in molecules such as N_2H_4 and H_2O_2. The dissociation energies for $N_2H_4 \rightarrow 2NH_2$ and $H_2O_2 \rightarrow 2OH$ are ~57 and ~51 kcal/mole, indicating that the catenated bonds in these molecules are much weaker than the hydride bonds. Thus hydrazine is endothermic while ammonia is exothermic, and H_2O_2 is considerably less exothermic than H_2O. The thermochemical data are incomplete for a comparable evaluation of second period elements, but it should be noted that the catenated bonds of these elements are also relatively weak; the dissociation energy for $Si_2H_6 \rightarrow 2\ SiH_3$ is approximately 51 kcal/mole,[5] while the bond energy for the P—P single bond in P_4 is 48 kcal/mole and dissociation energy for $H_2S_2 \rightarrow 2SH$ is 68 kcal/mole. That the strongest of these catenated bonds leads to reduced exothermicity is shown by the heats of formation of −4.8 kcal/mole for $H_2S(g)$ and −3.6 kcal/mole for $H_2S_2(l)$; note that the value for H_2S_2 is for the liquid phase and that the gaseous phase would be still more endothermic.

[3] Taylor, W. J., *J. Chem. Phys.*, 28, 625 (1958); Evans, W. H., U. S. National Bureau of Standards Report 7093, January, 1961.

[4] Coulson, C. A., "Valence," Oxford University Press, London, 1961

[5] These data as well as the following discussion were taken from Cottrell, T. L., "Strength of Chemical Bonds," 2nd ed., Butterworths, London, 1958.

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Uses of Electrical Discharges in Preparative Inorganic Chemistry

Energy in the form of heat and light has long been used to induce reaction between two or more otherwise stable compounds. It is only in comparatively recent times that energy in the form of an electrical discharge has been used. If an increasing voltage is applied between two electrodes in a gas at low pressure, a point is reached when the gaseous medium is transformed from a perfect insulator into an almost perfect conductor. In this state its molecules are broken down to the conducting species, ions, and the non-conducting species, atoms, and radicals, all of which are reactive. As the gas passes from the discharge region, the reactive species can combine to produce molecules different from the starting material. This article reviews the preparation of some unusual compounds using one of the three types of discharge:

(1) *Glow Discharge at Low Pressure.* The electrodes are actually placed in the gas under study so that on applying the breakdown voltage a current of several milliamps flows. The voltages used are in the range 1000–2000 volts.
(2) *Silent Electric Discharge.* The electrodes are separated from the gas (and each other) by an insulating material such as glass, thus even at the breakdown voltage of the gas very little current flows. The applied voltages normally lie between 5000 and 10,000 volts.
(3) *Microwave Discharge.* Absorption of microwave energy at the resonance frequency of a cavity through which the gas passes breaks bonds; the fragments recombine to form new molecules. The microwave power used is often in the region of 100 watts.

The very nature of these methods (the passing of gases through the reactive zone of the discharge) confines them to volatile compounds formed from elements of low atomic weight. In some cases discharges have been used to laboriously pioneer the properties of unique compounds until the results of such work have stimulated an intensive search for more convenient methods of their preparation.

Glow Discharges

Discharges have been used quite extensively in boron chemistry since the preparation of diborane by Schlesinger and Burg in 1931 revolutionized the study of the boron hydrides. Until that time these hydrides were prepared by a tedious method involving the acid-hydrolysis of kilogram quantities of magnesium boride which gave rise to only a few grams of the hydrides; the preparation and purification took several weeks to accomplish. With the new discharge method up to 30 mmoles of diborane (almost a gram) could be isolated in an hour. Mixtures of hydrogen and boron trichloride in the proportion 12:1 were passed at 20 mm pressure through a high voltage discharge maintained between water-cooled copper electrodes. Under these conditions the boron trichloride was reduced (*1*), possibly according to the equations:

$$BCl_3 + 3H_2 \rightarrow BH_3 + 3HCl$$

$$2BH_3 \rightarrow B_2H_6$$

Some of the diborane reacted with excess of the boron trichloride to form the spontaneously inflammable chlorodiborane:

$$5B_2H_6 + 2BCl_3 \rightleftharpoons 6B_2H_5Cl$$

A diagram of the discharge cell is shown in Figure 1. The hydrogen was bubbled through liquid boron trichloride held at low temperature (−40°) causing some of it to be vaporized and carried through the cell. By controlling the temperature of the liquid chloride it was possible to regulate the composition of the gas mixture for a given flow rate of the hydrogen. Once out of the discharge zone the exhaust gases were rapidly quenched in liquid nitrogen to freeze out the diborane, chlorodiborane, hydrogen chloride, and excess boron trichloride.

This illustrates a point to be used frequently in later years: viz., the unstable and often highly reactive products of a discharge must be swept clear of the hot discharge and quenched at low temperature as quickly as possible. However, the reactants must remain in the discharge for a period sufficiently long to undergo transformation and so the flow rate in a preparation such as that of diborane is somewhat critical. This is shown by the fact that essentially the same apparatus

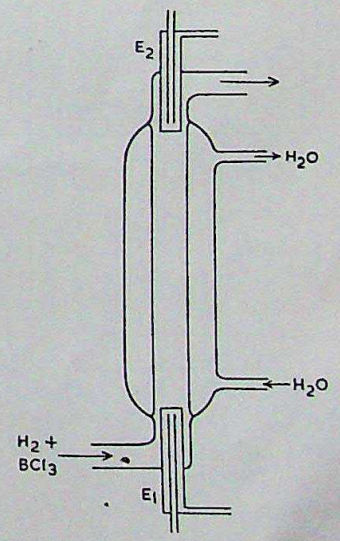


Figure 1. Water-cooled discharge tube used for the preparation of diborane.

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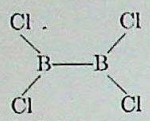
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(using a different flow rate) can be used for the preparation of elemental boron.

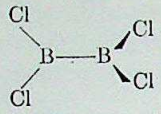
By employing a mercury discharge instead of one using copper electrodes, Schlesinger was later able to prepare significant amounts of diboron tetrachloride from boron trichloride (*2*):

$$3BCl_3 + 2Hg \rightarrow Hg_2Cl_2 + B_2Cl_4$$

this substance, the first simple compound to be made which contained a boron-boron bond (I), had previously been observed only in minute quantities (*3*).



Ia Solid state.



Ib Liquid and gaseous states.

Figure 2 shows a discharge cell similar to that used by Schlesinger, who noticed that no diboron tetrachloride was formed if the temperature of the cell was kept below 12° (below which temperature mercury has negligible vapor pressure) and postulated without further evidence that mercury vapor was directly responsible for the reduction of the boron trichloride:

$$2Hg(gas) + 2BCl_3 \rightarrow Hg_2Cl_2 + 2BCl_2$$

$$2BCl_2 \rightarrow B_2Cl_4$$

This preparation illustrates another method of passing gases through a discharge. The boron trichloride was placed in a trap on one side of the discharge cell and held at −78° (at which temperature its vapor pressure is reduced to 4 mm). By cooling a similar trap on the far side of the cell to −196° a steady transfer of material through the discharge zone was attained, the unstable diboron tetrachloride being condensed, along with excess of boron trichloride, in the 196° trap. The yield per passage of boron trichloride was only 1% so that the process had to be repeated, manually, many times. Improvements in the technique have rendered the process automatic by holding the boron trichloride at −78° and circulating the vapor through the discharge using a mercury diffusion pump or an automatic Töpler pump (*4*).

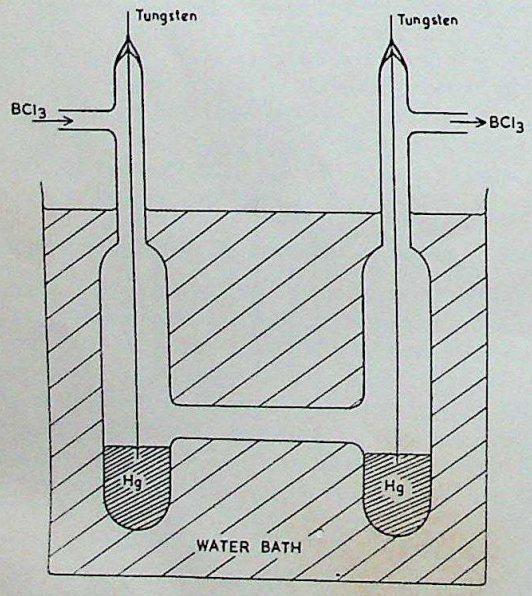
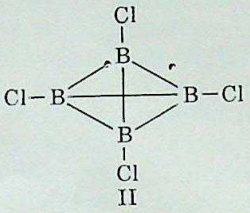


Fig. 2. Mercury discharge cell used for the preparation of diboron tetrachloride. It is shown immersed in a stirred temperature-controlled water bath.

For many years this has been the only known method for preparing diboron tetrachloride; the yields are low and amount to only 150–200 mg per hour under optimum conditions. Very recently other methods for its preparation have been described; but the yields, where quoted, have still been exceedingly poor.

Two other boron subchlorides are also formed as by-products during the discharge preparation of diboron tetrachloride. The very rare compound tetraboron-tetrachloride, B_4Cl_4 (II), is obtained as volatile yellowish crystals,



II

at the rate of 1–2 mg per day and is readily removed from the diboron compound by fractionation. Although its chemistry promises to be interesting (*5*) the exceedingly small quantities yet obtainable preclude an adequate study. As the preparation of diboron tetrachloride proceeds, the interconnecting walls of the apparatus become coated with a yellow monochloride, $(BCl)_x$; this has been stated to be a 2-dimensional polymer but its properties have not been studied.

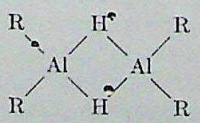
The discharge formation of diboron tetrachloride has been discussed in some detail since with only slight modifications of the technique it is possible to isolate other X_2M-MX_2 compounds (e.g., diboron tetrabromide (*6*), diphosphorous tetrachloride (*7*)[1] and dinitrogen tetrafluoride (*8*)) by reduction of the corresponding trihalide. It might be mentioned that boron trifluoride and phosphorus trifluoride are unaffected by passage through such a discharge.

Another interesting compound containing a boron-boron bond, decaborane-16, has recently been made by streaming a mixture of hydrogen and pentaborane-9 through a glow discharge struck between copper electrodes (*9*). The decaborane-16 is formed by loss of one molecule of hydrogen, at the apex positions, between two molecules of pentaborane-9 the remaining B_5H_8 units then unite

$$2B_5H_9 + H_2 \rightarrow B_{10}H_{16} + 2H_2$$

to give a boron-boron bond but still retain their individual tetragonal pyramidal structures, Figure 3.

Hydrides of other members of Group III of the periodic table have been prepared using similar methods. Thus hydrogen and the aluminum trialkyls combine when streamed through a glow discharge to give the tetra-alkylalumanes, $R_4Al_2H_2$, which probably contain bridging hydrogen atoms (*10*):



[1] For later work using a copper discharge see (*34*).

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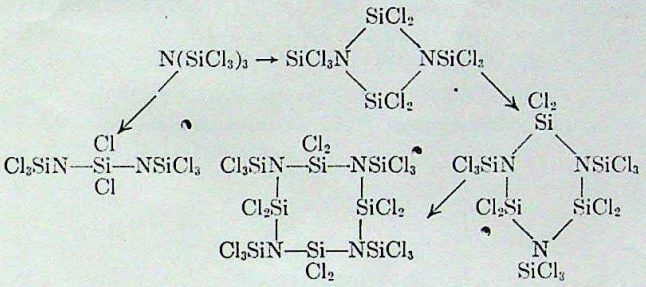
Similar products, $Ga_2H_2R_4$, have been stated to be formed from hydrogen and the gallium alkyls. They undergo a disproportionation equilibrium in which digallane is one product:

$$3Ga_2H_2R_4 \rightarrow 4GaR_3 + Ga_2H_6$$

The equilibrium can be displaced to the right by the addition of a trialkylamine, NR_3', which complexes with the gallium alkyl and leaves the digallane intact (*11*):

$$GaR_3 + NR_3' \rightarrow GaR_3 \cdot NH_3'; \quad R = Et, Me$$

Even very inert molecules such as nitrogen gas can be persuaded, by use of discharges, to enter into chemical combination. Thus when a mixture of nitrogen and silicon tetrachloride, $SiCl_4$, is streamed through a glow discharge, tris-trichlorosilylamine $N(SiCl_3)_3$ results. Other oily liquids and crystalline solids were isolated from the products, and they were shown to originate from the tris-trichlorosilylamine by loss of silicon tetrachloride. Cyclic and chain structures were given to these compounds (*12*):



When the discharge products are especially unstable the discharge tube may be built directly into a low temperature bath to freeze out the desired compound immediately as it is formed. This technique has been applied successfully to the preparation of the exceedingly labile trioxygen difluoride, the discharge being set up between copper electrodes in a vessel completely immersed in liquid oxygen, Figure 4. By streaming a 3:2 mixture of oxygen and fluorine through the discharge, 3–4 g per hour of the blood-red O_3F_2 can be obtained, even though it begins to decompose at temperatures as low as 115°K (*13*):

$$2O_3F_2 \xrightarrow{-158^\circ} O_2 + 2O_2F_2$$

For many years the action of a glow discharge on mixtures of sulfur vapor and sulfur dioxide was believed to give sulfur monoxide, SO (*14*). However it has been shown that the product is disulfur monoxide and that gases of composition SO are in fact mixtures of disulfur monoxide and sulfur dioxide. Sulfur monoxide is known in other systems at high temperatures and so it is possible that it does occur in the exhaust gases of the glow discharge. However, a careful search (*16*) showed that if it is present at all, it must polymerize in less than three seconds to disulfur monoxide and sulfur dioxide:

$$3SO \rightarrow S_2O + SO_2$$

Figure 5 shows the type of apparatus favored by workers in this field. Dry sulfur dioxide enters the system just above the level of molten sulfur in a heated reservoir and carries sulfur vapor with it on its path through the discharge. In order to maintain the discharge tube free from solid sulfur its temperature must be held about 20° above that of the reservoir by means of an electrically heated outer jacket. Disulfur monoxide can be stored in a clean vacuum apparatus for several hours at room temperature as long as the pressure is not allowed to rise above about 40 mm. Above this pressure, sulfur and sulfur dioxide are rapidly produced:

$$2S_2O \rightarrow 3S + SO_2$$

Silent Electric Discharges

The preparation of ozone from gaseous oxygen is a classical and well-known example of the use of this type of electrical discharge. Most of the reactions to be encountered are polymerizations; the gases may be either streamed through the discharge vessel or allowed to remain there indefinitely when the products are deposited as involatile solids or liquids on the vessel walls.

More recently the method has been applied with success to the preparation of higher hydrides of boron,

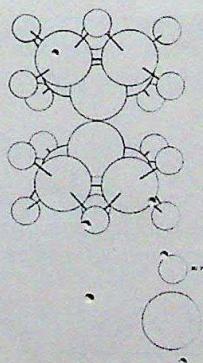


Figure 3. Structure of decaborane-16.

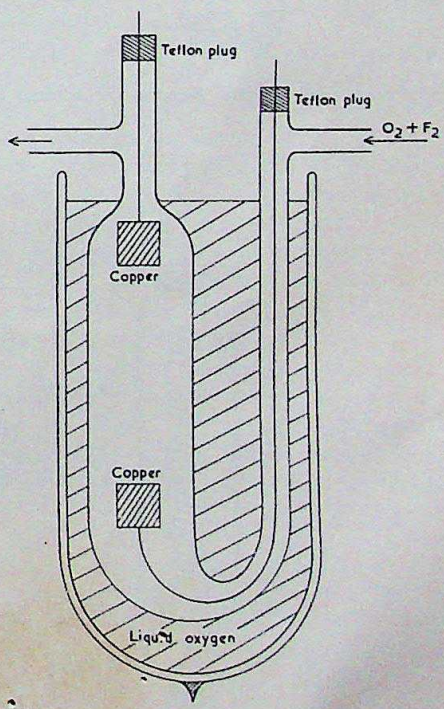


Figure 4. Discharge tube, immersed in a Dewer of liquid oxygen, used for the preparation of trioxygen difluoride.

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manium and arsenic. When diborane (*17*) was passed through an ozonizer-type of discharge tube (Fig. 6), tetraborane (40% yield), pentaborane-9 (20%), pentaborane-11 (30%), hexaborane-10, and decaborane were formed. By far the most significant product was the hydride B_9H_{15} which at that time (1958) was the first new boron hydride to be isolated since Stock's day, despite much intensive research. Enough of this enneaborane was isolated for the structure to be determined (*18*). Furthermore in the same study mass spectrographic evidence was obtained for both a hepta- and an octaborane. Other workers using a similar apparatus produced mass spectrographic evidence of a new, very unstable hexaborane, B_6H_{12} (*19*).

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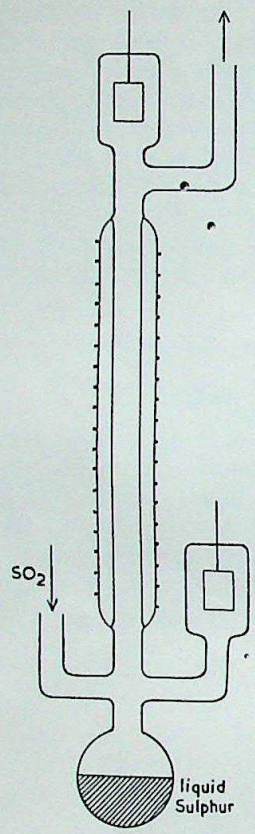


Figure 5. Apparatus used for the discharge preparation of disulfur monoxide.

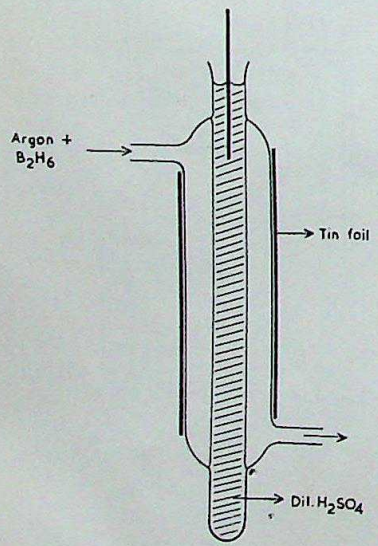
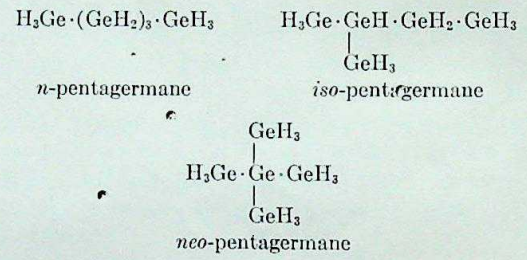
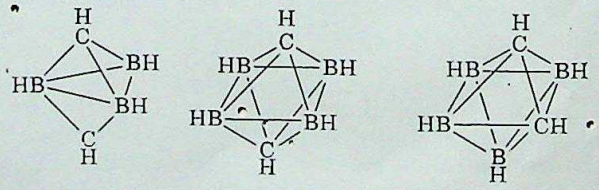


Figure 6. Simple form of silent electric discharge vessel used in studies on the cracking of diborane.

Diarsine, As_2H_4, was thought to be formed when arsine, AsH_3, was passed through a silent discharge, but the exceedingly unstable product could not be characterized with certainty (*20*). Monogermane was found to give higher germanes up to Ge_9, the yield of each falling off drastically with increase in molecular weight (*4*). The discharge tube was held at −78° for the duration of the experiment and the monogermane, at a pressure of about 30 cm was circulated through it with a Töpler pump. Under these circumstances all the higher germanes, except digermane, were frozen out on the walls of the discharge tube. After a run the products were fractionated on a vacuum line to remove di-, tri-, and tetragermane. The remaining germanes were then subjected to vapor phase chromatography and identified tentatively by retention times and by infrared and nuclear magnetic resonance studies. A large number of isomers, analogous to those of the paraffin hydrocarbons were postulated, e.g., the three pentagermanes:



Mixed carbon-boron hydrides, $B_nC_2H_{n+2}$, called the carboranes are novel products arising from the action of a silent discharge on mixtures of pentaborane-9 and acetylene (*22*). Little detail has yet been given regarding their preparation,[2] but their postulated structures, Figure 6, make them of great interest, although the apparent lack of acceptor power of the boron atoms is disappointing. The B—H bonds however do exchange with B_2D_6.



The effects of a silent discharge on the boron halides have been studied by many workers. Boron trifluoride and trichloride are not affected; the tribromide on the other hand produces bromine and boron monobromide (*23*):

$$xBBr_3 \rightarrow (BBr)_x + xBr_2$$

The corresponding monochloride, of unknown structure, results as a yellow film when diboron tetrachloride is quantitatively decomposed under static conditions (*23*):

$$xB_2Cl_4 \rightarrow (BCl)_x + xBCl_3$$

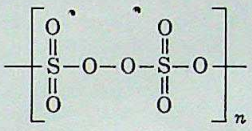
[2] See ref. (*35*).

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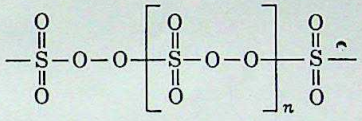
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Peculiar solids result when boron trifluoride or trichloride are subjected to a silent discharge for long periods in the presence of carbon monoxide. These have formulas corresponding roughly to BX_3-2CO, although their structures are unknown. The BCl_3 complex does not form chloride ion on treatment with water, the aqueous solution having a consistency like that of egg-white which demonstrates the polymeric nature of the compound (*24*).

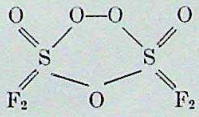
An equimolar mixture of oxygen and sulfur dioxide, when passed through a silent discharge tube held at −30°, gave a hard, transparent film of disulfur heptoxide, S_2O_7 (*25*). This polymer, which liberates iodine quantitatively from a neutral solution of potassium iodide, was given the structure



In later work (*16*) it was discovered that by discharging mixtures which contained a high oxygen: sulfur dioxide ratio a solid could be produced which analyzed to $SO_{3.9}$ and was thought to be mainly sulfur tetroxide, $(SO_4)_n$, mixed, possibly, with some disulfur heptoxide. This solid also showed oxidizing properties and a peroxy-structure was proposed:



In a related study (*27*) 1:1 mixtures of thionyl fluoride, SOF_2, and oxygen were subjected to a silent discharge at −50°; distillation of the liquid product yielded SOF_2, SO_2F_2, and two new compounds, $S_2O_5F_4$ and $S_2O_6F_4$. The $S_2O_5F_4$ melted at −95° and decomposed at −20° into sulfuryl fluoride and oxygen. It was considered to be monomeric and assigned a five-membered ring structure:



Continuing their study to the fluorides of Group V the same school of workers subjected phosphorus trifluoride/oxygen mixtures to a silent electric discharge at −75° and produced an exceedingly unstable compound $P_7O_{10}F_{15}$; the products of decomposition depended on the temperature (*28*):

$$P_7O_{10}F_{15} \xrightarrow{-38°} POF_3 + PF_5 + (PO_2F)_x$$

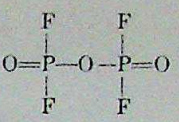
$$P_7O_{10}F_{15} \xrightarrow{-25°} POF_3 + PF_5 + P_2O_3F_4 + (PO_2F)_x$$

$$P_7O_{10}F_{15} \xrightarrow{0°} POF_3 + P_2O_3F_4 + (PO_2F)_x$$

The oxyfluoride, $(PO_2F)_x$ is a white, very deliquescent powder which decomposes quantitatively at 500°:

$$(PO_2F)_{4n} \rightarrow nP_2O_5 + P_2O_3F_4$$

The $P_2O_3F_4$, a liquid at room temperature, was considered to be the fluoride of pyrophosphoric acid and given the structure:



Microwave Discharges

This type of discharge has been little used in preparative inorganic chemistry. The apparatus consists simply of a quartz tube which passes through a tuned resonance cavity in a microwave bridge. When a gas at low pressure is passed through the tube, energy is absorbed and a glow discharge is produced. The preparation of small quantities of diboron tetrachloride has been achieved with this apparatus (*29*),

$$2BCl_3 \rightarrow Cl_2 + B_2Cl_4$$

the chlorine being removed by fractional distillation. Further studies showed that the accompanying glow discharge contained spectral lines which could only be attributed to BCl (and not BCl_2) radicals (*30*). This might suggest a two stage reaction:

$$BCl_3 \rightarrow BCl + Cl_2$$

$$BCl + BCl_3 \rightarrow B_2Cl_4$$

A similar experiment using germanium tetrachloride produced digermanium hexachloride (*31*):

$$2GeCl_4 \rightarrow Ge_2Cl_6 + Cl_2$$

Later, the same workers showed that the yield of hexachloride could be improved by placing a bronze wool plug at the end of the discharge zone (*34*).

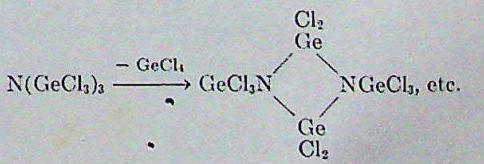
Phosphorus trichloride on the other hand did not produce diphosphorus tetrachloride (as it had in the mercury glow discharge) but disproportionated into red phosphorous and phosphorus pentachloride (*32*).

$$5PCl_3 \rightarrow 2P + 3PCl_5$$

However, if the gases issuing from the discharge are passed over bronze wool, CuCl and small amounts of P_2Cl_4 can be isolated (*34*).

That high energies are encountered in microwave discharges is convincingly demonstrated in the case of sulfur tetrafluoride, SF_4. Though hydrolytically unstable this compound shows high thermal stability and is only decomposed to the extent of about 1% after several hours at temperatures between 500–1000°C, the product being sulfur hexafluoride. When sulfur tetrafluoride is passed through a microwave discharge, there is a 59% conversion to the hexafluoride (*33*). Sulfur hexafluoride and chlorine give small amounts of sulfur chloride pentafluoride, SF_5Cl (*32*).

Mixtures of germanium tetrachloride and nitrogen, under the influence of the microwave discharge, gave oily products which readily lost germanium tetrachloride and were thought to be tris-trichlorogermylamine derivatives analogous to the silicon compounds (*32*):



During the discharge experiments the silica tube becomes very hot which apparently makes this type of

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discharge rather unsuitable for the study of reactive unstable compounds. More interesting results might be obtained if the resonance cavity and the silica reaction tube could be held in a low temperature bath without too great a loss of microwave energy.

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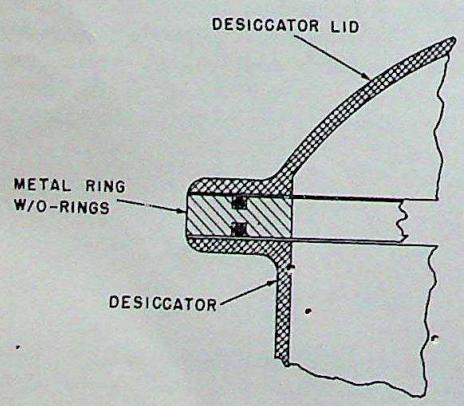
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Modification of a Vacuum Desiccater

In order to facilitate the removal of vacuum desiccator lids a simple device was constructed to eliminate the difficulty normally encountered in this step. Although simple in appearance this device has proved to be extremely helpful in application.

An aluminum ring (see figure) was machined such that its od and id corresponded to that of the ground surface of the desiccator. Into this ring were machined two O-ring grooves, one on each of the flat surfaces of the ring. This ring was then fitted with O-rings and inserted between the ground surfaces of the desiccator and its lid. During evacuation the O-rings are compressed until the flat surfaces of the ring contact those of the lid and desiccator. After the pressure inside of the vacuum desiccator has been increased to atmospheric pressure, the lid may be lifted easily from the surface of the O-ring. By cutting the grooves with different radii so that the top groove in the ring does not lie directly over the bottom groove, the thickness of the ring may be reduced.



A more desirable design would be to have the O-ring groove formed into the ground surface of the desiccator during its fabrication.

The technique described here has also been used to facilitate the removal of the belljar housing the new Ainsworth vacuum balance. Ainsworth is now supplying this modification with a matching belljar for purchasers of their earlier vacuum balances.

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The Variation of Vapor Pressure with Total Pressure

It is common knowledge that a volatile liquid, confined under the pressure of an inert gas, has a higher vapor pressure than when confined under the pressure of its own vapor. The relation between the total pressure and the vapor pressure is almost always derived by imagining the liquid to be confined in a closed cylinder with a piston, the head of which is permeable only to the vapor of the liquid. Only the vapor is then present on the other side of the piston head. The criterion of equilibrium, $dF = 0$, is then applied and the familiar relation

$$dP_{vapor}/dP_{liquid} = V_{liquid}/V_{vapor}$$

first derived by Poynting,[1] is obtained.

There are two difficulties encountered in teaching this topic according to the above approach. First, the student must visualize a piston head which is permeable to vapor but not to liquid—an unrealistic model. Secondly, the criterion of equilibrium, $dF = 0$, is applied to a system which is *not* at constant total pressure and therefore not at complete equilibrium. If he has learned that the condition $dF = 0$ is to be applied at constant temperature *and* total pressure, he will be confused. The following simple derivation avoids both difficulties; and the use of an inert, insoluble gas approximates better the conditions under which this phenomenon is usually experienced.

Consider a closed system containing the liquid (A) in equilibrium with a gas phase containing the vapor of A and an inert, insoluble gas. At equilibrium $\mu_A' = \mu_A$, so, for a virtual displacement, $d\mu_A' = d\mu_A$, where the primes refer to the liquid phase and the quantities without primes refer to the gas phase. Now, since

$$\mu_A' = f(T, P) \text{ and } \mu_A = f(T, P, X_A),$$

X_A being the mole fraction of A, and P and T the total pressure and temperature of both phases,

$$d\mu_A' = (\partial\mu_A'/\partial T)_P dT + (\partial\mu_A'/\partial P)_T dP \qquad (1)$$

and

$$d\mu_A = (\partial\mu_A/\partial T)_{P,\,X} dT + (\partial\mu_A/\partial P)_{T,\,X} dP + (\partial\mu_A/\partial X_A)_{T,\,P} dX_A \qquad (2)$$

But

$$(\partial\mu_A'/\partial P)_T = V_A' \text{ and } (\partial\mu_A/\partial P)_{T,X} = \bar{V}_A$$

Furthermore, if the gas is ideal,

$$\mu_A = \mu_A^\circ + RT \ln f_A = \mu_A^\circ + RT \ln p_A$$

so

$$(\partial\mu_A/\partial X_A)_{P,\,T} = RT(\partial \ln p_A/\partial X_A)_{P,\,T} = RT/X_A$$

since $p_A = X_A P$, where f_A is the fugacity of A and p_A its partial pressure at the total pressure P. Equating the right-hand sides of (1) and (2), imposing the condition of constant temperature ($dT = 0$), recognizing that $\bar{V}_A = RT/P$, and substituting for the partial differential coefficients yields

$$V_A'dP = (RT/P)dP + (RT/X_A)dX_A = RTd \ln P + RTd \ln X_A = RTd \ln p_A = (RT/p_A)dp_A \qquad (3)$$

Therefore

$$dp_A/dP = V_A'p_A/RT \quad \text{or} \quad d \ln p_A/dP = V_A'/RT$$

This relation is valid if the gas phase is ideal and if the gas is insoluble in the liquid. If, however, the gas (B) is soluble,

$$\mu_A' = f(T, P, X_A')$$

and equation (1) will have the additional term

$$(\partial\mu_A/\partial X_A')_{T,\,P} dX_A'$$

For a gas which obeys Henry's law it can be shown that

$$dp_A/dP = \bar{V}_A'p_A/RT - p_A/kX_A' \qquad (4)$$

where $k = dp_B/dX_B'$, the Henry's law constant for B in A. If the gas is only slightly soluble $X_A' \cong 1$, $\bar{V}_A' \cong V_A'$, and we have

$$dp_A/dP = V_A'p_A/RT - p_A/k$$

which is effectively the same as equation (3), since the last term is usually negligible.

Actually, there have been few experimental studies of the effect of high pressures on the vapor pressure of liquids, and the results of different investigators do not always agree. Among these may be mentioned the systems H_2-H_2O, N_2-H_2O and N_2-liquid hydrocarbons.[2–4] Bartlett's investigations[2] with water, for example, show that, although in the absence of inert gases the water content of the equilibrium vapor at 50° is 83 mg/l, under a total pressure of 200 atm of hydrogen it is raised to 95 mg/l. When nitrogen at 200 atm is used, the water content is 126 mg/l. At total pressures of 400 atm, hydrogen and nitrogen give water contents of 102 and 148 mg/l. The values predicted by equation (3) are 94 and 108 mg/l for total pressures of 200 and 400 atm, respectively. Thus equation (3) is valid for hydrogen at 200 atm but not for hydrogen at 400 atm, and it fails for nitrogen at both pressures. The chief cause for this failure does not

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appear to lie in the use of V_{H_2O}' instead of $\bar{V}_{H_2O}'$, for even at 400 atm the two are nearly equal, because of the small solubility of both gases. In fact, the use of equation (4) to include the effect of the solubility of the gas in the liquid makes no significant improvement. The real cause of the failure lies in the non-ideality of the gas mixtures, which does not permit equating $\bar{V}_A$ to RT/P or f_A to p_A, as was done in the derivation of equation (3) above. One may even say that in the light of available data the latter relation, although widely quoted in textbooks, is only of theoretical interest in this sense: As soon as the effect of total pressure on vapor pressure becomes large enough to be of importance, it can no longer be relied upon to give anything but a qualitative prediction of the effect. Satisfactory predictions can be expected only by eliminating the assumption of ideal behavior in the gas phase, and thus by not replacing V_A by RT/P or f_A by p_A. One then obtains, for only slightly soluble gases,

$$dX_A/dP = (V_A' - \bar{V}_A)/RT(\partial \ln a_A/\partial X_A)_{P,T}$$

the use of which requires more thermodynamic data on gas mixtures than are generally available.[5] Deviations from ideal behavior arise, of course, from intermolecular forces, and attempts have been made to correlate these with the experimental results.[6]

[5] For a method of handling such data the reader is referred to the paper of Dodge, B. F., and Newton, R. H., *Ind. Eng. Chem.*, 29, 720 (1937).

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Rigorous Derivation of the Kinetic Equation for Ideal Gas Pressure

The simple derivation of the pressure formula $PV = {}^1/_3\Sigma mc^2$ in the kinetic theory of gases proceeds from a consideration of the change in momenta at the wall of the freely moving gas molecules in a cubic container. Although this method leads very simply to the correct gas pressure, it leads to an incorrect value for the average number of collisions per second per unit area made by molecules of the gas. This limitation is most easily overcome, though with considerable loss of generality, by a consideration of a spherical[1] container. The other proofs of the pressure formula have the shortcomings of mathematical[2] or conceptual[3,4] difficulty in that it may be difficult to directly form an idea of the physical process considered.

The method developed by Clausius[5,6] for treatment of problems in kinetic theory is especially useful when there are intermolecular forces to be taken into account. The method is so very general and mathematically elegant that its mastery may be considered worthy of its apparent difficulty. In fact, except for the integration of the virial, there are no overbearing mathematical difficulties in it, and it stands well in comparison to some of the other proofs.[2] If a simplification of the mathematics is available there is no reason why the Clausius method should not be used with students for the derivation of the pressure formula of a gas. Its use will help to focus attention on intermolecular forces in gases and their mathematical treatment. We shall give a simplification of the evaluation of the virial of Clausius which was advantageously used with a class of fair mathematical ability. True enough, mathematicians abhor any proofs which involve argument from figures. But, this can hardly be objected to from a teaching point of view. We shall also outline an evaluation of the virial which, we think, is more elegant than that often given,[4] but we do not claim it to be a very simple proof. It is given to bring out the difference between the mathematician's approach and the simplified teaching approach.

Since the motion of any molecule in a gas is governed by Newtonian laws, we have

$$X = m\ddot{x},\ Y = m\ddot{y},\ Z = m\ddot{z} \qquad (1)$$

where X, Y, and Z are the components of the total force acting on a gas molecule having the coordinates x, y, z, and mass m. Multiplying (1) by x, y, and z, respectively, we have:

$$xX + yY + zZ = m(x\ddot{x} + y\ddot{y} + z\ddot{z}) \qquad (2)$$

Since

$$\frac{d}{dt}(x\dot{x}) = \dot{x}x + (\dot{x})^2$$

from (2)

$$xX + yY + zZ = m\frac{d}{dt}(x\dot{x} + y\dot{y} + z\dot{z}) - m(\dot{x}^2 + \dot{y}^2 + \dot{z}^2)$$

$$= \frac{1}{2}m\frac{d}{dt}\left[\frac{d}{dt}(x^2 + y^2 + z^2)\right] - mc^2 \qquad (3)$$

where

$$c^2 = \dot{x}^2 + \dot{y}^2 + \dot{z}^2$$

is the velocity of the molecule.

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[2] Pease, R. N., J. Chem. Educ., 16, 366 (1939).

[3] Jeans, J., "Kinetic Theory of Gases," Cambridge, 1940, chap. 3.

[4] Glasstone, S., Textbook of Physical Chemistry, Macmillan, 1940, p. 244.

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The term $(d/dt)\ (x^2 + y^2 + z^2)$ physically corresponds to the rate of change of the (distance)^2 of the molecule from the origin. As the molecule moves about, this continually fluctuates in value; but there is no tendency to a steady increase or decrease. As such, if we sum over all the molecules of the gas, since the molecules are moving at random

$$\Sigma \frac{d}{dt}\left[\frac{d}{dt}(x^2 + y^2 + z^2)\right] = 0 \tag{4}$$

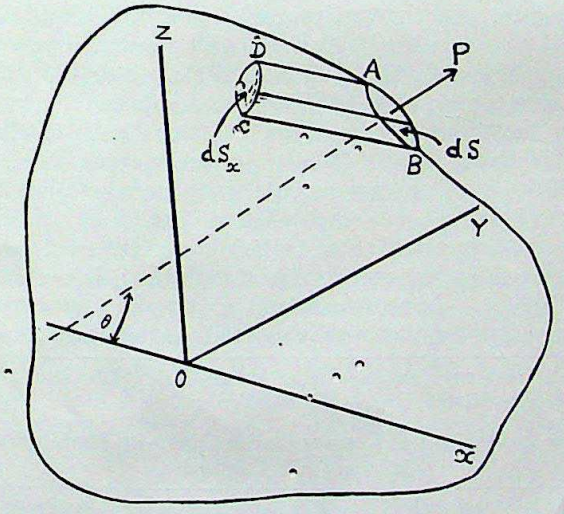
Thus, equation (3) becomes on halving,

$$-\frac{1}{2}\Sigma(xX + yY + zZ) = \frac{1}{2}\Sigma mc^2 \tag{5}$$

Equation (5) is the virial equation of Clausius, while the left hand side is called the virial.

X, Y, Z, are perfectly general forces which act on a molecule at x, y, z. These will involve intermolecular forces as well as forces that arise when molecules collide with one another or with the wall of the containing vessel. For an ideal gas, it is assumed by definition, that there are no intermolecular forces. Since we are interested in the pressure exerted by the gas molecules on the wall, we need to consider only forces that arise when molecules collide with the wall of the container.

Let the angle between the x axis and the direction of the gas pressure P, acting on the surface element dS be θ (see diagram). If X^s, Y^s, Z^s, be the sum of all the forces acting along the x, y, and z directions respectively, and exerted by the surface element on all the molecules colliding with it,



$$-x^s = P\cos\theta \cdot dS, \text{ etc.,} \tag{6}$$

the negative sign indicating that the force exerted by the element on the molecules is in the opposite direction to the gas pressure.

If the projection of dS on the yz plane be dS_x, since P is normal to dS, equation (6) becomes,

$$-X^s = PdS_x$$

similarly,

$$-Y^s = PdS_y, \quad -Z^s = PdS_z \tag{7}$$

$$\therefore -(xX^s + yY^s + zZ^s) = xPdS_x + yPdS_y + zPdS_z \tag{8}$$

The term dS = volume of the element $ABCD$ (see diagram)

$$\therefore \int xPdS_x \text{ for all } dS = P\int xdS_x = PV \tag{9}$$

where V is the volume of the container. P could be takenout of the integral sign since it is the same throughout, for all elements. Hence, from equations (8) and (9),

$$-\Sigma(xX^s + yY^s + zZ^s) = \frac{1}{2}P(\int xdS_x + \int ydS_y + \int zdS_z)$$
$$= \frac{1}{2}P(3V)$$

where the summation sign and the integral signs go over all the surface elements. Now,

$$\Sigma(xX^s + yY^s + zZ^s)$$

where the summation is carried over all the surface elements $= \Sigma(xX + yY + zZ)$ where the summation is carried out for all the molecules.
Hence

$$-\Sigma(xX + yY + zZ) = -\Sigma(xX^s + yY^s + zZ^s) = \frac{3}{2}PV$$

Therefore, from equation (5), $\frac{3}{2}PV = \frac{1}{2}\Sigma mc^2$ leading to

$$PV = \frac{1}{3}\Sigma mc^2$$

which is the required result.

This result can be obtained from the virial equation by the following vectorial method.

If P is the pressure on the surface element dS, the thrust on it due to the pressure is $Pd\mathbf{S}$. This would be equal and opposite to the sum of the forces X, Y, Z, acting on the molecules colliding with $d\mathbf{S}$.

If, as before, X^s, Y^s, and Z^s are the sum of the forces acting on all the molecules that strike the surface element dS, along the x, y, z, directions respectively,

$$-X^s = Pd\mathbf{S}\cdot\mathbf{i}, \quad -Y^s = Pd\mathbf{S}\cdot\mathbf{j}, \quad -Z^s = Pd\mathbf{S}\cdot\mathbf{k}$$

where **i, j, k,** are the unit vectors along the x, y, and z directions respectively. Hence

$$-(xX^s + yY^s + zZ^s) = xPd\mathbf{S}\cdot\mathbf{i} + yPd\mathbf{S}\cdot\mathbf{j} + zPd\mathbf{S}\cdot\mathbf{k}$$
$$= P\mathbf{r}\cdot d\mathbf{s}$$

where $$\mathbf{r} = i\mathbf{x} + j\mathbf{y} + k\mathbf{z}$$

Hence, summing up for all surface elements

$$\frac{1}{2}\Sigma(xX^s + yY^s + zZ^s) = -\frac{1}{2}P\int \mathbf{r}\cdot d\mathbf{S}$$

Now, by Green's theorem

$$\int \mathbf{r}\cdot d\mathbf{s} = \int(\nabla\cdot\mathbf{r})dV = 3\int dV = 3V$$

since

$$\mathbf{r} = i\mathbf{x} + j\mathbf{y} + k\mathbf{z}, \quad \nabla\cdot\mathbf{r} = 3$$

Also, as before

$$\Sigma(xX^s + yY^s + zZ^s) = \Sigma(xX + yY + zZ)$$

Hence

$$\Sigma(xX + yY + zZ) = -\frac{1}{2}\Sigma mc^2 = -\frac{3}{2}PV$$

$$\therefore PV = \frac{1}{3}\Sigma mc^2$$

is the required result.

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Using Tantalum and Platinum-clad Tantalum Electrodes for Depositions

Electrodeposition experiments are widely used in undergraduate courses in quantitative analysis. Examples are the determinations of copper and nickel in alloys (*5*), silver and copper in solders and alloys (*2*), and copper in a variety of materials (*9*). The latter is one of the simplest and most accurate electrodeposition determinations.

The high cost of buying and maintaining platinum electrodes[2] has led several investigators to try tantalum substitutes. Müller (*7*) developed tantalum coated copper, silver, and aluminum electrodes which are then coated with platinum and used as the anode in anodic oxidation processes. Strock and Lukens (*10*) recommended tantalum as a satisfactory substitute for a platinum cathode in the electrodeposition of copper but had difficulty with oxides on the surface.

Rosenblatt and Cohn (*8*) described the preparation of platinum-clad tantalum, and suggested its use as an anode in the production of peroxy compounds, or in the electrolysis of chlorides without danger of corrosion. This paper describes student electrodeposition experiments in which platinum-clad tantalum electrodes have been used, with particular emphasis on copper deposition. Conditions and limitations are also presented.

Copper Deposition

The platinum clad tantalum expanded mesh electrodes were made to our specifications by Metals and Controls Corporation, Attleboro, Massachusetts.[3] The cathode consisted of a cylinder ($1^3/_8$- × $1^1/_4$-in. diameter) with the stem spot welded to the outside. The anode was a cylinder (1- × $^5/_8$-in. diameter) with the stem spot welded to the inside and offset to the center with two 90° bends so that it could be rotated with the stem as the axis. Over-all height of each electrode was $4^1/_2$ inches, including stems.

The preparation of platinum-clad tantalum is described in a patent by Rosenblatt and Cohn (*8*). After the bonding process the foil consists of a thin outer layer of pure platinum (0.00025-in. thick in this application), an inner layer of platinum-tantalum alloy, and a base of pure tantalum (0.00975-in. thick). The foil is pierced and expanded to give the mesh-like material (200 openings per square inch) used for the electrodes. Since the platinum coats only one side of the tantalum, the platinum sides of the anode and cathode were made to face each other. The 0.055-inch diameter wire stems were solid platinum for one set of electrodes and solid tantalum for the other set. The unclad tantalum electrodes were of similar construction, but of a finer mesh size, having about 750 openings per square inch.

Procedure. After dissolution of the copper sample in 6 ml of 1:1 sulfuric acid, water is added to give a volume of about 100 ml, and then 1 ml of freshly boiled concentrated nitric acid is added as a cathode depolarizer. Electrolysis is carried out at 60–90° in tall-form beakers. After electrolyzing 15 minutes at 2 amperes about 0.5 g of urea is added and the deposition is continued for another 45 minutes. The cathode is then rinsed with distilled water, rinsed with alcohol, dried for 2–3 minutes in a 105–110° oven, and weighed.

To determine whether platinum-clad tantalum electrodes can be used with an accuracy comparable to platinum electrodes, a stock solution of electrolytic copper was prepared and aliquots analyzed by the above procedure. In the analysis of a solution containing 0.6711 g copper, the Pt-clad Ta electrode with Ta stems gave values of 0.6711, 0.6712, 0.6704, and 0.6704 g for an average yield of 99.95%; the same solution analyzed with similar electrodes with Pt stems gave 0.6703, 0.6706, 0.6707, and 0.6704 g for an average yield of 99.91%. Similar experiments with conventional Pt electrodes gave an average yield of 99.92%.

To further establish the reliability of the electrodes, copper oxide ores[4] were analyzed with the results shown in Table 1. Approximately 3 g samples were used, giving 0.2–0.3 g of copper in most of the determinations.

[1] Candidate for the degree of Master of Science in the Evening Division.

[2] A pair of platinum electrodes costs $125–$250, depending on the weight and type of anode used. (August, 1962 quotation from Fisher Scientific Co., Philadelphia, Pa.)

[3] A pair of platinum-clad tantalum electrodes already fabricated costs $65–$75, depending on whether the stems are of unclad tantalum or of platinum wire. On the other hand, the material for a pair of electrodes costs only $15–$25, depending on whether tantalum or platinum wire stems are used. (Estimates based on quotation from Texas Instruments, Metals and Controls Division, Attleboro, Mass., June, 1960.) Fabrication of the electrodes is simple, since only spot welding is required.

[4] The ores were obtained from Thorn Smith, Chemist, 1347 North Main Street, Royal Oak, Michigan.

Table 1. Analysis of Copper Oxide Ores with Platinum and Platinum-Clad Electrodes

% Cu found with Pt-clad Ta electrodes Ta stems	Pt stems	% Cu found with Pt electrodes
7.38, 7.44 7.44, 7.41	7.42, 7.44 7.44, 7.44	7.47, 7.50 7.46, 7.46
Ave.: 7.42 *Assay:* 7.43	*Ave.:* 7.44 *Assay:* 7.43	*Ave.:* 7.47 *Assay:* 7.43
8.15, 8.16 8.13, 8.17 8.14	8.17, 8.18 8.19, 8.18 8.21	8.23, 8.18 8.23, 8.21
Ave.: 8.15 *Assay:* 8.19	*Ave.:* 8.19 *Assay:* 8.19	*Ave.:* 8.21 *Assay:* 8.19
13.86, 13.85 13.87, 13.86	13.96, 13.91 13.86, 13.91 13.93	13.95, 13.90 13.93, 13.94
Ave.: 13.86 *Assay:* 13.91	*Ave.:* 13.91 *Assay:* 13.91	*Ave.:* 13.93 *Assay:* 13.91

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All 39 analyses performed with the procedure given above are reported, with no values rejected. Most of the results agree with the reported value to better than 0.2% (relative). Standard deviations range from 0.01 to 0.04% Cu, with no significant differences among the three kinds of electrodes. The data in Table 1 shows that good results can be obtained with platinum-clad tantalum electrodes. The copper deposits on the platinum-clad tantalum electrodes were smooth, adherent, and salmon-red colored, but were slightly duller than the deposits on platinum electrodes. Even the small amount of deposit on the unclad tantalum stem had a smooth and adherent appearance.

Table 2 shows the changes in weight incurred by the various kinds of electrodes during electrodeposition studies. Later investigation showed that most of the weight loss occurs during the 5-10 minute interval in which copper is stripped from the electrodes by immersion in 1:2 nitric acid. Although the various tantalum electrodes undergo a greater change in weight than do platinum electrodes, the losses can be considered negligible.

Discussion of Electrodeposition Conditions. With platinum electrodes, the copper samples could be electrolyzed at room temperature and at up to 3 amperes current, with deposition being complete in 30–45 minutes. With platinum-clad tantalum electrodes these conditions were unsatisfactory. The current had to be maintained at 2 amperes or less, otherwise flaky and loosely adherent deposits of copper were obtained, and results were consistently low. Keeping the current at about 2 amperes gave denser and more adherent deposits, but deposition was incomplete even after $1^1/_2$ hours. It was found that increasing the temperature to 60–90° gave complete deposition in 1 hour at 2 amperes. Increasing the current to 3 amperes at the elevated temperature often gave quantitative recovery in 45 minutes, but the deposits were too flaky to be reliable. Therefore, 2 amperes was adopted as the maximum deposition current. Urea was used in the procedure to decompose nitrogen oxides, which would delay the deposition or tend to oxidize the copper (*5*).

Earlier work had established that quantitative results could be achieved with platinum-clad tantalum at room temperature if currents were maintained at about 1 ampere for 3–4 hours, but this procedure was rejected as being too time consuming for a student experiment. Nevertheless, it is felt that deposition times slightly longer than an hour might make results even more quantitative than those reported above, particularly when tantalum stems are used with the platinum-clad tantalum electrodes.

Unclad Tantalum Electrodes for Copper Deposition

Strock and Lukens (*10*) were the first to point out that tantalum could be satisfactorily substituted for platinum as the cathode in the electrodeposition of copper, but they pointed out that the surface had to be kept free of oxide film. Recently, Abramova (*1*) used a tantalum cathode to separate polonium from other metals, and Weiss and Shipman (*12*) used a tantalum disk cathode in a plutonium separation. Early in this investigation attempts were made to use unclad tantalum for both anode and cathode in the electrodeposition of copper, but it was found that the electrical resistance of the electrodes was prohibitive. Even with 9–10 volts imposed between the electrodes, currents were in the order of 0.1 ampere or less, whereas with platinum-clad tantalum electrodes, currents of 1–2 amperes are obtained with 3–4 volts applied. Further, recoveries of only 20–30% copper were obtained after electrolyzing 2 hours. Müller (*7*) and Young (*13*) allude to the high electrolytic resistance of tantalum electrodes, and the latter reports that an oxide film is responsible. Van Muylder and Pourbaix (*11*) found that tantalum reacts with water to form Ta_2O_5 at all *p*H values, and that the oxide film protects tantalum from further corrosion from all acids except HF. Evidence for oxidation of the tantalum anode in copper deposition is shown in Table 2 by the gain in weight of the unclad tantalum anode.

Strock and Lukens used an abrasive to remove the oxide film from their tantalum cathode but the weight loss in this process was appreciable (*10*). Mears and Pine (*6*) indicated that an ammonia-trichloracetic acid mixture, useful in stripping copper from a tantalum cathode, was also effective in removing the oxide film. Studies in this laboratory using tantalum for both the anode and cathode indicated that an ammonia-trichloracetic acid mixture is inefficient for removing the film; even after a dozen cleanings the resistance was high and deposits were poorly adherent. A more efficient cleaner was found to be a mixture of HF and H_2O_2 (1 part 30% H_2O_2, 2 parts 48% HF, and 7 parts H_2O). A 7 minute immersion in this solution permitted a current of 0.5–1 ampere to pass upon applying 8–8.5 volts, but the copper deposits were flaky and loose, and yields were only 90–94%. An unclad tantalum cathode in conjunction with a platinum-clad tantalum anode gave a normal electrolytic resistance (3–4 volts gave currents of 1–2 amperes) and nearly quantitative recoveries of copper, but the deposits were still too flaky to be reliable. These investigations were not pursued further.

Platinum-Clad Tantalum Electrodes for Other Electrodepositions

Stability of the Electrodes. Hampel (*3*, *4*) has indicated that tantalum is inert to all acids except HF at temperatures usually encountered in industrial processes. Before attempting other determinations with the platinum-clad tantalum electrodes, this stability was

Table 2. Weight Changes of Electrodes after Copper Electrodepositions.

Electrode	Unclad Ta		Pt-clad Ta				Pt	
			Ta stems		Pt stems			
	Anode	Cathode	Anode	Cathode	Anode	Cathode	Anode	Cathode
Weight at start (g)	4.2150	5.5045	6.4296	11.8335	6.6815	10.2886	8.0011	11.0494
Net weight change (mg)	+1.7	−1.9	−2.1	−1.6	−1.9	−1.6	+0.3	+0.1
No. of depositions	6	13	10	10	14	15	10	9
Ave. weight change per deposition (mg)	+0.3	−0.2	−0.2	−0.1	−0.1	−0.1	+0.03	+0.01

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reaffirmed under electrolysis conditions. First, the electrodes were immersed for at least 15 minutes in warm (*ca.* 70°C) solutions of 1 : 2 HNO_3, 1 : 2 HCl, 60% $HClO_4$, and both acid and alkaline ammonium acetate-ammonium nitrate mixtures (the latter solvents are recommended for the electrodeposition of silver and copper (*2*). The loss in weight after each of these treatments was negligible. Next the stability of the electrodes was determined while electrolyzing blank solutions. The first blank consisted of a mixture of 15 ml of concentrated (60%) $HClO_4$, 30 ml of concentrated nitric acid, and 100 ml of distilled water. After electrolyzing 30 minutes at 2 amperes neither electrode had changed weight. A second blank consisted of an ammonium acetate-ammonium nitrate mixture (*2*), and electrolysis for 30 minutes each in alkaline and then acid solution at about 0.8 amperes resulted in negligible change in weight of the anode and cathode.

Silver from Silver-Copper Alloys. Deposition of silver from KOH-KCN solution with Slomin's procedure (*9*) gave yields as good as those with platinum electrodes; accuracy was high, and the silver coatings were smooth, white, and adherent. A trial of the platinum-clad tantalum electrodes by a class of 40 students with the ammonium acetate-ammonium nitrate procedure of Adams and Blaedel (*2*) gave a class median relative error of 0.3%, which was the same as the median relative error of another class of 30 students that used platinum electrodes.

Anodic Deposition of PbO_2. The anodic deposition of PbO_2 (*9*) was also attempted using platinum-clad tantalum electrodes. Recoveries of PbO_2 were incomplete at deposition voltages and times sufficient for quantitative deposition with platinum electrodes. Attempts to improve the yield by using higher voltages gave deposits that were poorly adherent, and losses by flaking occurred. On the other hand, deposition on a platinum anode with a platinum-clad tantalum cathode gave results that were as good as those obtained with two platinum electrodes.

Conclusions

Results have been presented to show that platinum-clad tantalum electrodes can be used for the deposition of copper and silver with about the same convenience, speed, and accuracy as platinum electrodes. In some cases, it may be necessary to electrolyze at slightly lower current densities than with platinum electrodes, but this disadvantage is more than offset by the greater mechanical strength and lower cost of the platinum-clad tantalum electrodes.

Even when deposition on platinum-clad tantalum electrodes gives poor results compared to deposition on platinum, it may be possible to use platinum-clad tantalum as the electrode on which plating does not occur.

Acknowledgments

The authors would like to thank the numerous undergraduate students and Donald A. Smith in particular for participating in preliminary studies with the various electrodes. Presentation of a pair of platinum-clad tantalum electrodes by Metals and Controls Corporation, and of unclad tantalum mesh by Fansteel Metallurgical Corporation is gratefully acknowledged.

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MCA Honors Six College Chemistry Teachers

The 1963 College Chemistry Teacher Awards of the Manufacturing Chemists' Association have been announced. The following medalists were chosen from nominations submitted by college and university presidents:

Ernest H. Swift, California Institute of Technology, Pasadena, California
Ernst Berliner, Bryn Mawr College, Bryn Mawr, Pennsylvania
Frank Hovorka, Western Reserve University, Cleveland, Ohio
Edwin O. Wiig, University of Rochester, Rochester, New York
Laurence E. Strong, Earlham College, Richmond, Indiana
Joseph D. Danforth, Grinnell College, Grinnell, Iowa

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S. D. Christian,
H. E. Affsprung and **C. Lin**
University of Oklahoma
Norman

Vapor Density Apparatus

Vapor density experiments, as performed in the undergraduate physical chemistry laboratory, are frequently inaccurate and time-consuming. The requirements that a known mass of vapor be contained in a known volume at known temperature and pressure, in the absence of stopcock grease, are quite demanding on the skill of the student and the quality of the apparatus.

We have devised a vapor density method, suitable for instructional or research use, that is both rapid and capable of considerable accuracy. The method has been tested on several vapors of known molecular weight.

Apparatus and Method

The apparatus is sketched in Figure 1. In preparing for a run, the 1-liter flask *F* is evacuated through tube *B* while the mercury in the tube is maintained at a level slightly below the sintered-glass disc *A*. The mercury level may be adjusted by manipulating the Teflon-plug stopcock *C* (not greased) and the three-way stopcock *D*, thereby either forcing mercury into or out of the reservoir *E*. When the pressure in *F* has been reduced to a sufficiently low value (as indicated by the closed-end manometer *M*), the mercury level in *B* is raised to a height about 1 cm above the disc *A*. Stopcock *C* is securely closed, air is allowed into tube *B* and the standard taper cap *G* is removed.

A run may now be made by introducing a known volume of a volatile liquid through the disc *A*, using a graduated volumetric pipet.[1] After the addition of each increment of liquid, the pressure and temperature are measured. With liquids such as benzene, cyclohexane and carbon tetrachloride, a total volume of several tenths of a ml may be introduced at room temperature before saturation is reached. Upon completion of a set of measurements, the mercury level in *B* is lowered, and flask *F* is again evacuated. For non-associating vapors, it is not necessary to evacuate the system to zero pressure, since a correction can be made for the pressure of residual gases or vapors in the system at the start of the experiment.

Results

The results of a series of runs on benzene, carbon tetrachloride and cyclohexane vapors are shown in Figure 2. The total pressure increment, Δp, resulting

[1] This is accomplished by filling the pipet to a given mark, wiping the tip to remove adhering liquid, and inserting the tip of the pipet through the mercury until it contacts the disc. Since the pressure inside the flask *F* is less than the pressure in the pipet, liquid will be sucked through the disc. When a sufficient volume has been added, the pipet is withdrawn and the final liquid level is noted. Occasionally a small amount of liquid mercury enters the pipet as it is withdrawn—this must be drained before the final liquid level is measured. A 0.1 ml graduated pipet was used in all the experiments described here.

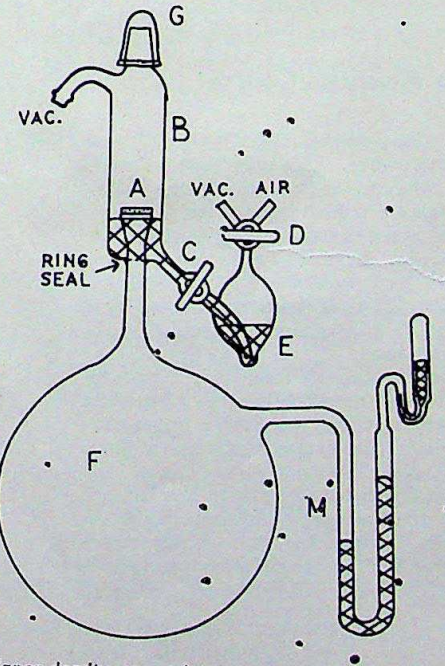


Figure 1. Vapor density apparatus.

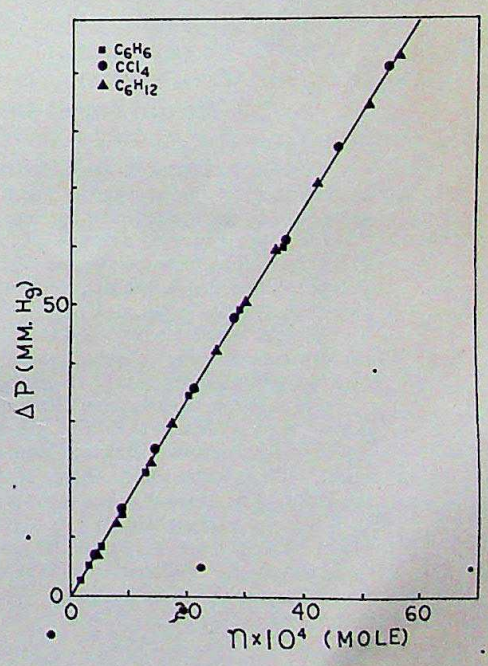


Figure 2. Benzene, carbon tetrachloride, and cyclohexane vapors at 23.6 ± 0.2° C. Line represents least squares fit of data.

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from the cumulative addition of n moles of liquid at 23.6 ± 0.2°C is plotted versus n. From the plot it can be seen that nearly the same curve is defined by data for each of the liquids. By a least squares method, values of the slope m in the equation

$$n = m\Delta p \qquad (1)$$

were calculated for each vapor, as well as σ, the standard deviation in n, assuming all the error to reside in the n values. Also calculated were the values of m and the standard deviation in n for all points considered collectively. These constants and the values of the system volume, V, calculated from the ideal gas equation, are reported in Table 1. Examination of the

Table 1. Curve Parameters for Equation (1)

System	$m \times 10^4$ (mole mm Hg^{-1})	$\sigma \times 10^4$ (mole)	V (ml)
Benzene	0.6060	0.12	1122
Carbon tetrachloride	0.6008	0.22	1112
Cyclohexane	0.6028	0.14	1117
All systems together	0.6035	0.19	1116

table reveals that the standard deviation in n is nearly the same for all points collectively as for each system by itself. The slopes, m, lie in the range $m = 0.6035 \times 10^{-4} \pm 0.003 \times 10^{-4}$ mole mm Hg^{-1}, which corresponds to a net uncertainty in the system volume of about ±6 ml. The standard deviation in n corresponds to a standard deviation in the volume of liquid added through the pipet of about 0.002 ml.

It should be noted that the system volume actually varies slightly as the mercury level in the manometer changes, and a correction for this can be made if necessary. However, if several vapors are to be studied over a wide range of pressure, it is adequate to calibrate the system using vapors of known molecular weight in the same pressure range.

Discussion

Several advantages of this apparatus recommend it for use in studying vapors at pressures less than one atmosphere. First, no greased parts need be used in the entire apparatus. Second, liquid mixtures of known composition may be investigated as easily as pure liquid compounds. Third, it is possible to thermostat the entire apparatus below the sintered-glass disc A. This is particularly important in studies of the vapor densities of associating compounds, as for example carboxylic acids. In such experiments it is desirable to vary the temperature while a known mass of vapor is present in the system. Further, calibration is simple—a sample of a known liquid is first introduced and measured, whereupon an unknown sample may be added immediately without evacuating the system.

Provided the system is adequately thermostated, vapor pressures of pure liquids or dew-point pressures of mixtures may be determined. Successive increments of the liquid or liquid mixture are added as before until condensation occurs. The vapor pressure or dew-point pressure is identified as the pressure at which a break occurs in the Δp versus n curve. It has been demonstrated that the dew-point curve for a binary system may be utilized in the calculation of activities and activity coefficients[2,3]; hence the present apparatus might be applied in studying liquid-vapor equilibria.

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Weight Burets for the Quantitative Analysis Course

The doll's nursing bottle, described in a previous note (this Journal, 36, 290 (1959)), can be used as a weight buret in the beginning quantitative analysis course. This polyethylene bottle costs only 10 cents, cannot be broken, and is easily cleaned. Since water does not wet the plastic tip, the drops delivered average 35 to the gram. These drops are half the size of drops from a glass tip. Thus, a more precise titration is possible. Also, since the water does not wet the polypropylene nipple, the titrant does not spread out over the tip. This eliminates an "evaporation-from-the-tip" error.

Weight burets do not need to be corrected for the density change of the titrant caused by a temperature change. Calculations are done by "weight titer." The titrant is standardized in terms of milligrams of constituent sought for each gram of titrant used.

Considering the merits of the weight burets, it seems strange that this method for titrations is not more generally taught in the beginning course. Our experience has been that students report the same precision and accuracy using the weight burets as they get with a volumetric buret. When given a free choice of the two methods for doing a titration, our students without exception have elected to use weight burets.

The use of weight burets could cause a troublesome traffic back-and-forth to the balance room. To eliminate this we have placed dial torsion balances in the working laboratory. With these automatic balances weighings can be done in less than 15 seconds. One balance serves 20 students without congestions. These balances are sensitive to 5 mg, so weighing precision is better than 0.1%.

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Bethany, West Virginia

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Conversion Grids for Ternary Systems

Composition expressed on a weight per cent basis must frequently be converted into other composition parameters which do not have a 1:1 correspondence with the weights per cent. A common example of this is mole per cent. The reverse problem also exists when mixtures of specified mole percentages must be prepared by weighing operations. The present work is framed in terms of these specific conversions, although the methods are more generally applicable. Such conversions may involve a number of mathematical operations. For example, that from weight per cent to mole fraction for but one component in a ternary system requires four divisions and a sum. Conversion tables are not practical for this purpose because of the three composition variables. When the conversions must be performed repeatedly, as in continuing work with a given system, the cumulative labor is considerable.

The conversion grids described below may be used to advantage under these conditions. They are easily constructed and used, and effect a significant saving in labor. Their use reduces the five operations noted just above, for example, to two sums and a division. The basis of the grids and their construction are described. Specific illustrations of conversion are given in terms of the system benzene—carbon tetrachloride—*n*-hexadecane (B-C-H).

Grid Basis

Assume the weights per cent of the i components B, C, H to be p_B, p_C, p_H, and their molecular weights M_B, M_C, and M_H. *Per 100 g of mixture* there will be n_B, n_C, and n_H moles of the components and n_T total moles. Thus

$$n_T = n_B + n_C + n_H \tag{1}$$

$$n_i = \frac{p_i}{M_i} \tag{2}$$

$$100 = p_B + p_C + p_H \tag{3}$$

Consider a particular straight line in a weight per cent ternary diagram. Whether the diagram is of the equilateral or right-angled triangular type, it is possible to relate two of the weights per cent by an equation of the form, using B and H for example,

$$p_H = mp_B + b \tag{4}$$

where m and b are the constants of the slope-intercept form of the straight line equation. Substitution for each of n_i in equation (1) in terms of equation (2), and use of equations (3) and (4) to eliminate p_C and p_H in the resulting equation yields n_T as a function of p_B,

$$n_T = Rp_B + S \tag{5}$$

where

$$R = \frac{1}{M_B} + \frac{m}{M_H} - \frac{m+1}{M_C} \tag{6}$$

$$S = \frac{100 + b}{M_H} - \frac{b}{M_C} \tag{7}$$

From equations (6,7) it is evident that S and R are constant for a particular straight line, or that equation (5) is linear. Now for a set of parallel straight lines R is constant by equation (6) because m is constant. Moreover, from equations (5,7)

$$\left[\frac{\Delta n_T}{\Delta b}\right]_{p_B} = \left[\frac{\Delta n_T}{\Delta S}\right]_{p_B}\left[\frac{\Delta S}{\Delta b}\right]_{p_B} = \frac{1}{M_H} - \frac{1}{M_C}$$

Thus there is a constant incremental change in n_T between every adjacent pair in a set of equidistant parallel lines. For the particular set where

$$m = M_C\left[\frac{1}{M_B} - \frac{1}{M_H}\right] - 1$$

by equation (6) R reduces to zero and n_T is a constant, equal to the S fixed by equation (7). To summarize, there may be superimposed upon a weight per cent diagram a series of equidistant parallel constant n_T lines, which are suitable for linear interpolation of intermediate n_T values. In the above the interpolation has been developed in a vertical direction in the ternary diagram.

Also superimposable is a scale of the various n_i, which are proportional to the corresponding p_i by equation (2). Thus a point on the weight per cent ternary diagram may also be interpreted directly in terms of n_i and n_T, yielding the mole fraction by a ratio determination.

Reasoning parallel to that above shows that conversion from mole fraction to weight per cent is also possible by this approach. That is, a weight per cent grid may be superimposed on a mole fraction ternary diagram.

Grid Construction and Use

Figure 1 shows the grid for conversion from weight per cent to mole fraction. Constant n_T lines have been constructed at intervals of 10 weight per cent in B along the vertical (B-C) axis. Figure 2 shows the grid for conversion from mole fraction to weight per cent. Lines of constant total weight per mole of mixture have been constructed at intervals of 0.10 mole fraction in B along the B-C axis. In actual use the two grids may be combined on a single plot; they have been separated here only for clarity. Tables 1 and 2 list proportional parts useful for interpolation in Figures 1 and 2 respectively.

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Table 1. Interpolation from Weight Per Cent to Moles per 100 Grams of Mixture

Weight % increment	Moles B	Total moles
1	0.0128	0.0063
2	0.0256	0.0126
3	0.0384	0.0189
4	0.0512	0.0252
5	0.0640	0.0315
6	0.0768	0.0378
7	0.0896	0.0441
8	0.1024	0.0504
9	0.1152	0.0567

Table 2. Interpolation from Mole Fraction to Weight in Grams Per Mole of Mixture

Mole fraction increment	Weight B	Total weight
0.1	0.78	0.76
0.2	1.56	1.51
0.3	2.34	2.27
0.4	3.12	3.03
0.5	3.90	3.78
0.6	4.69	4.54
0.7	5.47	5.30
0.8	6.25	6.06
0.9	7.03	6.81

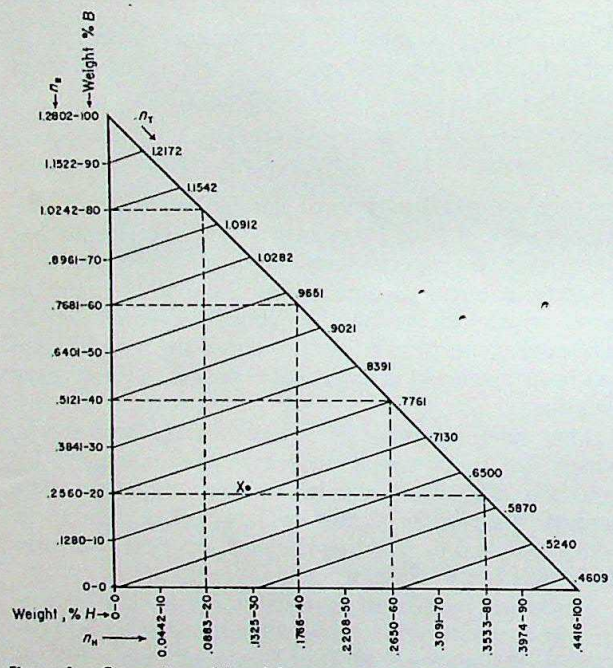


Figure 1. Conversion grid, weight per cent to mole fraction.

Example. Determine the mole fraction B in a mixture of weight percentages 23.2 B, 29.2 H, 47.6 C, corresponding to point x in Figure 1.

moles B:	total moles:	
0.2560	0.7130	
0.0384	0.0189	mole fraction B: 0.404
0.0026	0.0044	
0.2970	0.7363	

Example. Determine the weight per cent B in a mixture of mole fractions 0.461 B, 0.342 H, 0.197 C, corresponding to point y in Figure 2.

weight B:	total weight:	weight per cent B:
31.24	138.69	$100\,\frac{36.01}{143.76} = 25.0$
4.69	4.54	
0.08	0.53	
36.10	143.76	

In each example the result obtained with the grid differs by less than 1 unit in the last place from the result obtained by the detailed fundamental calculation. It is apparent that the concentrations of the other components of the system could also be converted by use of the grids.

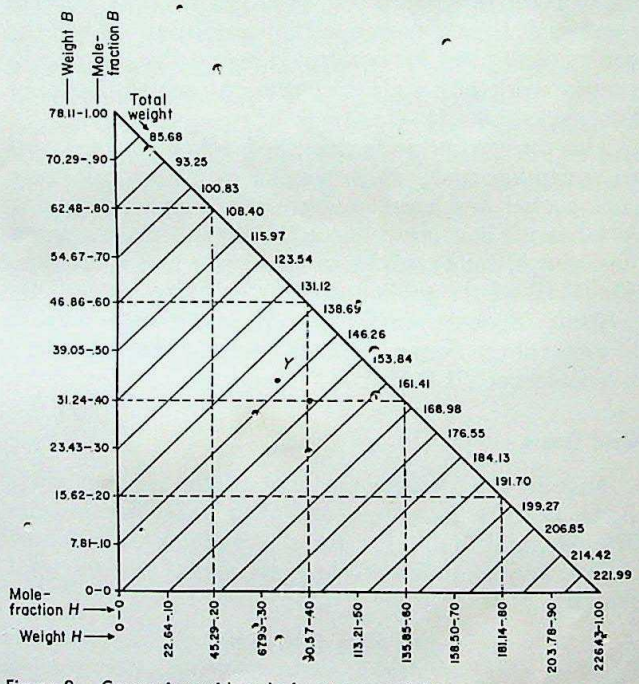


Figure 2. Conversion grid, mole fraction to weight per cent.

Erratum: Multicenter and Assisted Mechanistic Pathways

The article by R. E. Dessy and F. Paulik in the April, 1963, issue of THIS JOURNAL (40, 185 (1963)) contained an incorrect identification of two substitution processes. In the center of the right-hand column on page 190, the reaction should read:

$$\text{X—Y} + \text{E—N} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \underset{\text{E—N}}{\overset{\text{X—Y}}{\uparrow}}{}^{k_2} \rightarrow \text{Product} \qquad S_F{}^a$$

Five lines below the reaction should read:

$$\text{X—Y} + \text{E—N} \overset{k_1}{\rightarrow} \text{Product} \qquad S_F{}^2$$

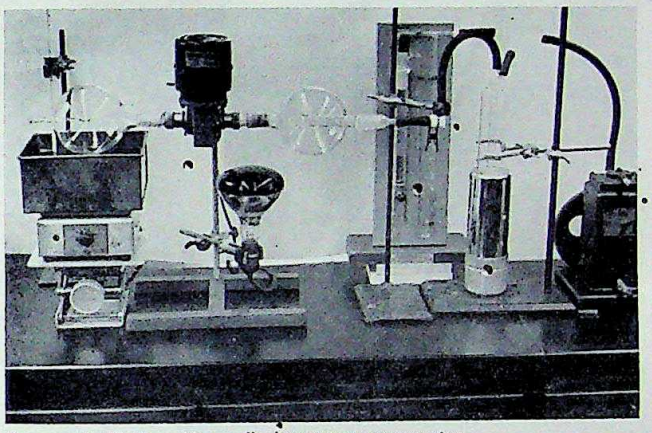
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M. Benton Naff and
William Spector
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Vacuum Distillation with an all Glass Rotary Evaporator

In the purification of high boiling compounds by vacuum distillation an all glass rotary evaporator is useful. The apparatus illustrated in the drawing is commercial equipment with slight modification. The set-up consists of a round-bottom flask with a ₹10/30 thermometer joint sealed to the bottom, a Buchler rotary evaporator and glass sleeve (₹24/40 teflon coated male joints), a Rinco solvent recovery flask, and a ₹24/40 female adapter. The Buchler teflon ball and socket vacuum outlet is used to connect the adapter on the condensing flask to a cold trap of chloroform–carbon tetrachloride–dry ice. The cold trap is connected to the manometer and vacuum pump via a T-tube.



Vacuum distillation with an all-glass rotary evaporator.

In aligning the equipment it is essential to angle the set-up so the evaporator flask is slightly higher than the condensing flask. This aids drainage in case the distilled compound solidifies in the connecting tube and must be melted by an infrared lamp. In some cases it may be necessary to cool the condensing flask with tap water. A pressure of 1 mm can be attained with the apparatus described.

This equipment is very useful in the purification of glycols, e.g., in the distillation of ethylene glycol or diethylene glycol, following treatment with sodium borohydride and in the purification of 2-butyne-1,4-diol. On standing in a closed container in the dark, butynediol gradually undergoes decomposition. A dark tarry product forms. Therefore, the glycol must be purified just prior to use in synthesis. In the apparatus described, 100 g of butynediol (General Aniline and Film, distilled grade), mp 48–56°C and amber-brown in color, was distilled at 1–2 mm pressure and a temperature of 104–106°C (oil bath temperature 125 ± 5°C). The distillation required twenty-five minutes and yielded 94.5 g (94.5%) of white solid, mp 56–58°C., lit. 58°C.[1]

[1] REPPE, W., ET. AL., *Ann.* **596**, 25–38 (1955); *C. A.*, **50**, 16773*f*.

Chem Ed

LETTERS

To the Editor:

The article "Ion Strength, Ion Association and Solubility" by Gerald Corsaro (THIS JOURNAL, **39**, 622 (1962)) presents some interesting ideas for experiments and discussion, but we should like to offer the following comments and observations:

1. Dr. Corsaro corrected his ionic strength values for the presence of undissociated calcium sulfate, but he considered this salt to be completely dissociated in the calculations of equilibrium molarities. In saturated solutions of such an electrolyte one expects the "molecular form" to exist in relatively constant concentration, and by considerations of solubility data we estimate a value of about 0.007 *M* for undissociated calcium sulfate. When this is taken into account in the calculation of K_d' (as defined by Corsaro) the value of the latter is 0.65 instead of 0.85.

2. The value (0.0049) of the dissociation constant for calcium sulfate used for the correction of ionic strength values refers to zero ionic strength but was applied under conditions ranging up to unit ionic strength. Because of the highly charged ions involved, one would expect this "constant" to change markedly with ionic strength.

3. Dr. Corsaro suggests that the formation of the complex $NH_4SO_4^-$ should be negligible. However, because of the high ammonium ion concentrations in his

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solutions most of the sulfate would be in this form. For example, taking 13 as the thermodynamic value of the $NH_4SO_4^-$ formation constant, we estimate the value to be about 3 in the 0.5 *M* ammonium salt solutions. This would mean that only one-third of the dissolved sulfate would exist as the free ion. Thus, although this has only minor consequence in the correction of ionic strengths, the effect on sulfate molarity is far from negligible.

However, it is interesting to note that because Corsaro's approach is based on comparison of calcium sulfate solubilities in ammonium chloride and ammonium perchlorate and because the ammonium ion concentration is high enough to be only slightly affected by the formation of $NH_4SO_4^-$, the effect does not show up in the final calculations of K_d'. We feel that this aspect should not be ignored in discussions with students.

4. In obtaining the thermodynamic values of K_d shown in Table 4, the Debye-Hückel equation should be used only with apologies. The uncertainties shown for the constant values are far smaller than seems reasonable.

5. This approach to the determination of the dissociation quotient can illustrate for the student the many complications, assumptions, and uncertainties inherent in such work, and hence the limitations of the indirect method. It would be unfortunate if an oversimplified model and treatment tended to conceal this more critical view.

Richard W. Ramette
John C. Marshall

St. Olaf, College
Northfield, Minnesota

To the Editor:

R. W. Ramette and J. C. Marshall express concern that the treatment of the data in the article may have been oversimplified tending to conceal a critical view of the real nature of the problem.

As they suggest in a private communication, the values of $(1-\alpha)S$ can be plotted against

$$\frac{\mu^{\frac{1}{2}}}{1+\mu^{\frac{1}{2}}}$$

and thus arrive at an alpha value in keeping with that of the dissociation constant at zero ionic strength, if the plotted values of $(1-\alpha)S$ are extrapolated to zero ionic strength. This value of alpha may then be shown to give 0.007 *M* for associated calcium sulfate remaining in solution. This value should then be subtracted from the found values of calcium sulfate in solution before making the calculations illustrated.

If one employs the latter procedure, the K_d' values would be changed somewhat from those listed in Tables 2 and 3, also the values for K_d listed in Table 4. The agreement between values for a given series of mixed salt solutions would, however, be retained as would the K_d values listed.

The use of the Debye-Hückel equation for calculating the K_d values may not normally be expected to yield values in good agreement over the range of ionic strengths listed in Table 4. The results listed, however, were obtained as illustrated and the agreement shown may in part be due to the choice of the relatively large ion size for calcium ion, and the assumption that the activity coefficients of the chlorocalcium and chloride ion species are identical.

It was my intention in submitting the data and methods of calculation used in the article to illustrate the complexity of solubility studies and the sensitivity of electrolytic behavior to ionic environment, and that the Debye-Hückel theories could serve as valuable guides in understanding electrolytic behavior. Certainly, the article and the data illustrate that solubility equilibria are more complex than one may anticipate if the factors illustrated are taken into account. The objections raised by Ramette and Marshall are valid ones and perhaps would better have served the purpose intended by the writer in submitting the article, if the more complete procedure suggested by them had been employed in the calculations.

Gerald Corsaro

University of Akron
Akron, Ohio

To the Editor:

In a previous letter to this Journal (38, 329 (1961)) we described the separation of barium-137m from its parent cesium-137 on a preformed precipitate of ammonium 12-molybdophosphate (AMP). We have recently used this technique to separate thallium-208 (Th-C'') from acidified thorium nitrate solution.

Thallium-208 is a beta emitter with a half life of 3.1 min and is useful for demonstration purposes or class practical work. The thorium nitrate solution can be used repeatedly if about 20 min is allowed after each separation for the thallium-208 to return to equilibrium.

A thin bed of approximately 120 mg of AMP is prepared as described in our previous letter. A solution of 5 g of thorium nitrate in 10 ml of 2 *M* nitric acid is poured through the AMP bed at a flow rate of 4–5 ml per min, using slightly reduced pressure. The bed is washed with 10 ml of 2 *M* nitric acid, sucked dry for about 30 sec, and the filter paper and the AMP carefully mounted for counting.

This normally gives us an initial count of approximately 1200 cpm under an end-window Geiger-Müller tube (GEC type GM 4). From the counting data a linear plot of log cpm versus time is obtained from which the half life is readily determined.

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R. D. Harding
S. J. Patel

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Leicester, England

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Division of CHEMICAL EDUCATION

American Chemical Society

The Visiting Scientists Program in Chemistry

One of the more ambitious programs being sponsored and directed by the Division of Chemical Education is now in its eighth year of operation. Although the membership of the Division is undoubtedly aware of the existence and probably something of the scope of the Visiting Scientists Program, some more detailed information may be of interest. From its original inception for college visits only, the program has expanded so that junior colleges are included, as well as selected high schools. Visits by distinguished chemists from foreign countries are now sponsored by a subcommittee functioning with the Visiting Scientists Program.

Planning by the committee (eight members appointed by the chairman of the Division of Chemical Education) was greatly facilitated two years ago when the National Science Foundation funded the program for a two-year period. Thus the 1961–2 budget was amended to extend through the academic year 1963. Some idea of the magnitude of the operation is gained from gross annual budget figures. The college program is operating on $41,000, the high school program on $24,300, and the foreign program on $28,400.

During the 1961–2 year 67 college and university teachers participated as visitors in the college program in approximately 300 visiting days. The total number of requests filled by the committee is but a fraction of the number of requests for visits. Financial as well as personnel limitations preclude granting more than about one-third of the requests. Each institution visited assumes the responsibility of food and lodging for the visitor and a small share of the travel cost. As of 1962–3 this share is common to all institutions at thirty-five dollars ($35.00). This plan for billing equalizes the cost to any institution regardless of geographic location. The college program operates under the direction of the chairman of the Visiting Scientist Committee, Professor D. J. Cook of DePauw University.

Fifty-three visitors representing teachers in colleges, universities, and selected high schools are currently participating in the high school program under the direction of Professor Joseph Danforth of Grinnell College. The visits are arranged through the local sections of the ACS. During the academic year 1961–2 155 days were spent in the high schools by these visitors. Every effort is made by the committee to honor all requests, though again, personnel limitations are a factor.

The foreign program operates at present (1962–3 academic year) under the directorship of Professor Kent Wilson of Tufts University. Professor L. Carroll King of Northwestern University served as director last year, the first of its existence. The planning for any given foreign visitor often must span a two-year period. The complexities of travel obviously are far greater in the foreign program than in the others. On occasion expenses of oversea travel are shared with or even borne completely by a university, government agency, or industry—greatly aiding the finances of the committee. Thus, outstanding contributors have been recruited on several occasions from the campuses of universities where those distinguished visitors were already "on the scene." In other instances members of the committee serving fellowship tenures in foreign countries bring back recommendations of suitable visitors: The ideal visitor, whether foreign or domestic, is not always easily obtained. Last year there were seven foreign visitors. Of the 108 institutions requesting visits from them, 53 were visited. A more or less typical situation is that a visitor covers a geographical area in a week or two, spending one or two days on a campus. Both formal and informal meetings are held during which philosophy, content of chemistry courses, and the research of the visitor's country are discussed.

College

Year	No. visitors	No. of institutions receiving announcements	No. of institutions requesting visit	No. of visits completed	% of requests filled
1960–1	65	1000 (approx.)	280	134	48
1961–2	60	1200 (approx.)	215	132	61
		High School			
1960–1	50	164	60	45	75
1961–2	50	164	55	55	100

From the feedback available to the Visiting Scientists Committee, it would appear that the objectives of the program—to strengthen and stimulate the chemical programs in colleges; to provide the chemistry staff and chemistry majors in colleges, especially small and junior colleges, with the contact with productive and creative chemists; and to aid in the motivation of able college and secondary school students toward careers in chemistry and chemistry teaching—are being expanded as well as more than fulfilled.

Robert C. Brasted
Treasurer of the Committee
University of Minnesota, Minneapolis

Division Program for Fall ACS Meeting—New York

September 9: A.M. General papers
P.M. Symposium: Cellulose and Polymer Chemistry
September 10: Symposium: Undergraduate Chemistry Curricula
September 11: General papers
September 12: Symposium: Advances in Instrumental Analysis

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Proceedings of the California Association of Chemistry Teachers

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Modern Geochemistry

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The geological sciences have developed rapidly during the past 15 years or so. In this development geophysics and geochemistry have emerged as major divisions of the sciences. One might even be so bold as to predict that in the future they will become dominant. What I will term classical geology will always be studied, for rooted in this aspect of geology are fundamental aspects of our concepts of time and change. In the early stages of the development of geology, as with most natural sciences, there was an essential period of descriptive data collection so that the broad features and boundaries of the problem could be assessed. During this period, there was certainly no lack of attempts at explanation, but once description becomes repetitive, and hence less stimulating, the question "how" must occupy more attention, and "how" in modern science demands experiment. The standard works of geochemistry appear as necessary, but rather dull catalogues of the analytical inorganic chemistry of the earth. While much of these data are inadequate, element analysis for its own sake is interesting fewer workers and the geochemistry of the early part of this century, as with the inorganic chemistry, has passed into a new physicochemical stage.

The scope of the geochemical problem in this physicochemical context is extensive. We are concerned with a chemical system containing a dozen or so dominant elements with lesser amounts of every element and isotope—something one might anticipate from examination of lifetimes of the nuclides. These elements are mixed in an environment where pressure varies from almost a perfect vacuum to over three million atmospheres, and temperatures range from below 0°C to at least 3000°C. As well, local variation in the gravitational field, stress, and partial pressures of volatile constituents must be considered. To understand our present situation and its evolution past and future requires a complex analysis of equilibrium states (classical thermodynamics), steady states (irreversible thermodynamics), and chemical kinetics. It is this general problem that makes up modern geochemistry. One thing is certain at the outset; except in very limited problems, answers will be approximate. But these answers will be fitting to the scale of the problem and should allow selection of a good model and rejection of the unreasonable. Perhaps the most important objective is that geochemical and geophysical studies should provide information on the broad features of the behavior of chemical systems over this extended range of physical conditions.

This paper summarizes a lecture delivered at the 1962 California Association of Chemistry Teachers' Conference, Asilomar, California.

Earth Models

Present earth models involve a rather thin outer crust (30 km ±) of granitic to basaltic composition, a crust dominated by the elements O, Si, Al, Fe, Ca, Na, K, Mg, Ti, H. Below the crust, the mantle extends to about 3000 kms and is composed dominantly of magnesium-iron silicates. The core, the outer part liquid and central part solid, is normally considered to consist of nickel and iron but recent considerations indicate that large amounts of light elements such as silicon may be present. About 99% of the entire earth can be considered to be made of Fe, O, Si, Mg, Ni, S, Ca, Al. Thus we have an oxygen deficient system, stratified in a varying gravitational field. The model appears reasonable when considered with respect to heats of formation of oxides (competition for the available oxygen) and gravitational stability of the resultant phases (*1*, *2*).

Perhaps it should be stressed that over the pressure range of the earth (3×10^6 bars) any reaction with even a small negative volume change may proceed at depth against a most unfavorable surface free energy. Thus a reaction with a small negative ΔV of 1 cm³/mole and a $\Delta G°$ of +24 kcal/mole will proceed at a million atmospheres. It is thus to be expected that structural modifications, energetically unfavored at the surface are quite feasible at reasonable depths, for the energy gain of one electron volt per cm³ is comparable with the energy of normal chemical bonds (1 ev/molecule = 23 kcal/mole).

To man, the crust is of most immediate importance; but crustal processes cannot be divorced from the interior, for convective processes in the core and mantle determine the majority of large scale crustal disturbances. In the crustal range, 1–20 kilobars pressure and temperatures not much above 1200°C, apparatus is now available to carry out many of the conventional experiments of physical chemistry. Cold pressures of near half a million atmospheres and 100,000 atmospheres at 2500°C have been achieved (*3*) in static apparatus. Limited data can be obtained using shock wave techniques, and, as an example, David and

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Hamann (*4*) have found a value for K_w of 10^{-3} in water compressed to 127 kilobars at 770°C. Let us consider very briefly some of the major areas where chemical and geological knowledge merge and where active geochemical research is in progress.

Analytical Chemistry

The determination of major and minor elements in the average rock is one of the most demanding exercises of analytical chemistry. Recent trends have been toward non-destructive, instrumental methods. Neutron activation techniques which allow minimal handling have led to superior values for the concentration of minor elements. X-ray spectrographic techniques are rapid and may eventually replace flame photometry for alkali metal determination. But perhaps the greatest advance in the geological context will result from the use of the electron probe (*5*). With this instrument it is possible to carry out a moderately precise analysis of an area of the order of 10^{-8} cm^2. For the first time, it is possible to ascertain whether a minor element is in true homogeneous solution in a host lattice or if it is present as a discrete phase along grain boundaries and imperfections. We can now expect considerable sharpening of concepts concerning the fractionation of minor phases in geological processes. Further, as minerals frequently show compositional zoning and diffusion phenomena, these can now be studied precisely.

Modern geochemical analysis may often include isotope analysis. For example, oxygen isotope fractionation (*6*) may provide information on temperatures of formation and may allow quantitative limits to be placed on the quantities of water involved in the deposition of vein minerals.

Inorganic Chemistry

Studies of mineral synthesis and crystal growth in hydrothermal systems (*7*, *8*) has led to interesting possibilities in preparative chemistry. Synthetic zeolites have been used as molecular sieves and there are many possible uses of synthetic silicate fibres, micas, etc. Even metals may be transported under suitable conditions.

Crystal or ligand-field theory which has recently had such important impact on transition metal chemistry has many important applications in mineralogy and petrology. A great number of common minerals are solid solutions containing transition metal ions. In the analysis of the thermodynamics of mixing, changes in the crystal field splitting as a function of composition is a source of a significant departure from ideality. In some cases these changes may explain the stability of mixtures (e.g., $(MgFe)SiO_3$), and lack of end member stability (e.g., $FeSiO_3$). In the process of transition metal separation from a complex silicate liquid, crystal field differences between liquid and solid again may play a large part in determining the distribution coefficients and fractional crystallization (*9*). As transition metal ions decrease in size when spin coupling occurs in a strong field, it may be anticipated that in the deeper levels of the earth, contraction will occur in iron silicates producing diamagnetic materials (*10*).

Complex ions must exist in the dense, high temperature solutions of many geological situations. Data on this subject is almost totally lacking at present; but when it is considered that vapors in equilibrium with solids increase in complexity with temperature (*11*) and that electrolyte solutions become molecular (*12*), it is clear that complex species are highly probable. Dickson and Tunell (*13*) have shown that the transport of HgS at low temperatures probably involves the $HgS_2^=$ complex. It is essential that we understand ion and molecule solvation in aqueous solutions. In fused salts also, complexing and polymerization must be important. Weill has studied the solubility of SiO_2 in fused Na_3AlF_6. In pure fused cryolite at 1010°C silica is almost insoluble; but as Al_2O_3 is added, the solubility reaches 60 wt% at 10% Al_2O_3. Clearly, some large molecular species is being formed.

Structural Chemistry

In a science dealing almost exclusively with solids, the X-ray crystallographer occupies a key position. Recent structural studies have indicated the common occurrence of order-disorder transitions in aluminosilicates. The Al-Si ordering and disordering processes are sluggish and this must be considered in the interpretation of calorimetric data. With a phase such as albite, $NaAlSi_3O_8$, heat capacity measurements will not provide true values for the stable amount of order except near the melting point. At all lower temperatures whatever state happens to be used will remain unchanged in the time of measurement. Also recently, silicates with more than one type of grouping (e.g., SiO_4^{4-} and $Si_2O_7^{6-}$) and with stacking disorders (in mica structures) have been recognized. The recognition of the structure of new modifications (e.g., SiO_2 in the rutile structure stable above 100,000 atmospheres) demands structural analysis.

Organic Chemistry

Studies of the organic constituents of rocks has led to the development of a so-called biogeochemistry. Just as inorganic materials bear the imprint of the physical chemistry of the crust, organic remains in fossils give some clues as to biological processes. Even the oldest rocks containing fossils, organic matter, amino acids, proteins, etc., may be preserved under suitable conditions. Organic deposits and biological processes are responsible for many economically significant processes.

Physical Chemistry

Classical thermodynamics provides the mainstay of most geochemical studies of heterogeneous equilibria. But in the laboratory, experimental times are at least 10^6 times too short to reproduce some crustal phenomena. Thus the study of rate processes is fundamental. In the study of heterogeneous processes, calorimetric data should be of great significance but the precision required to answer many geological questions is extreme and more often direct phase studies may provide superior free energy data.

The physical chemistry of solutions or mixtures is frequently significant. For example, the chemistry of processes in the oceans is largely a problem of ion activities in a mixed electrolyte solution; sulfide ore transport involves electrolytes, complex ions, and redox

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chemistry in a high P-T aqueous environment, and the formation of great masses of some rocks, many cubic miles in volume, requires knowledge of the behavior of silicate melts, many containing significant amounts of water. A beautiful example of a silicate water system is provided by the work of Kennedy, *et al.* (*15*) on the upper critical end point in the system SiO_2–H_2O. At this upper critical point a vapor phase containing 75 wt% silica is found (see Fig. 1).

In the high temperature chemistry of electrolytes significant data have recently been found by E. U. Franck (*12*). From conductance studies, Franck has shown that most conventional strong electrolytes such as HCl, NaCl, NaOH, are weak electrolytes in much of the region of the crust. Franck's estimates of K_w are shown in Figure 2 and some dissociation constants for electrolytes are listed in Table 1.

Heterogeneous Equilibria

The unravelling of the physicochemical history of crustal rocks has involved study of phase changes. As mentioned already, apparatus is available to carry out experiments over the entire crustal range. Nearly all significant minerals have been synthesized or could be synthesized. During geological processes, key reactions include hydration—dehydration equilibria, loss of CO_2, polymorphic inversions (first and second order), and more limited changes in oxidation states. Many lines of evidence indicate that local thermodynamic equilibrium is common in rocks and that changes representing response to the highest P and T are preserved. This preservation and lack of reversibility is partly due to most reactions requiring a solvent phase to proceed, a phase which may be present during loading and heating, but absent during subsequent unloading. The variables in this system include P-T, the partial pressures of volatile constituents in a pore phase, and stress. This array of variables could lead to a chaotic mineralogy if all were fully independent. But in the over-all picture, temperature and pressure are functions of depth; and at depth, porosity and permeability may be so low that a dehydration reaction only proceeds at a finite rate when the vapor pressure approximates the total pressure. Thus the same types of changes are repeated in constant patterns at different times and places. Most experimental work has been concentrated on solid-melt, hydration-dehydration, and polymorphic transitions. The melting points of most silicate systems are increased by inert pressure and decreased by water pressure. Eutectic compositions, transition points, and solid solution separations may all be changed by these variables. These data provide the limits on the regions where solids or liquids dominate. In the sub-liquidus region, which includes most of the crust, attention has mostly been focused on polymorphism and hydration reactions, the variables being

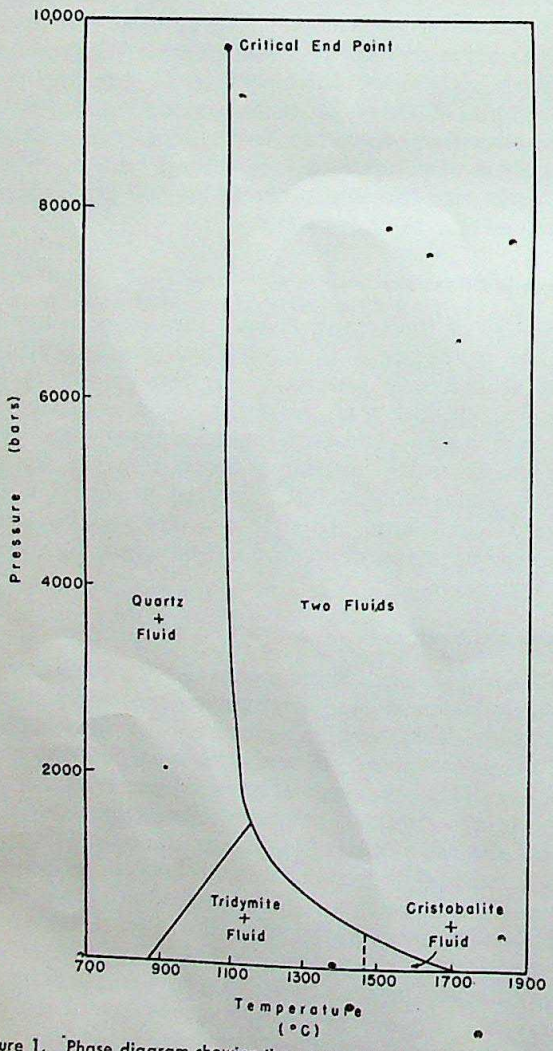


Figure 1. Phase diagram showing the upper critical end point. in the system SiO_2-H_2O after Kennedy, *et al* (*15*).

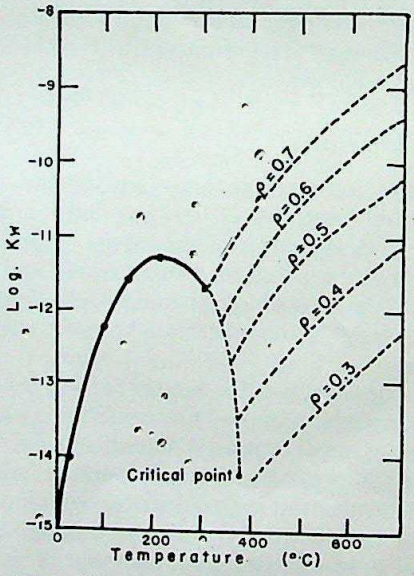


Figure 2. Variation of K_w with density (ρ) from estimates of Franck (*12*). The heavy line represents values for the liquid which have been directly measured.

Table 1. Dissociation Constants of Electrolytes in Water

Substance	T (°C)	Solvent Density (gcm^{-3})		
		0.3	0.5	0.7
KCl	450	3.6×10^{-5}	2.8×10^{-3}	4.0×10^{-2}
	650	6.3×10^{-6}	1×10^{-3}	...
	750	3.7×10^{-6}	...	...
KOH	400	9×10^{-5}	2.7×10^{-3}	1.5×10^{-2}
	600	0.8×10^{-5}	1.3×10^{-3}	1.3×10^{-2}
	700	0.4×10^{-5}	1.0×10^{-3}	...
HCl	400	4.0×10^{-6}	1.1×10^{-4}	7×10^{-3}
	600	1.8×10^{-6}	2.9×10^{-5}	1.0×10^{-3}
	700	0.7×10^{-6}	1.4×10^{-5}	...

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P_{H_2O} and T, while water provides the necessary solvent for reaction.

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The most common method of study of a complex silicate equilibrium has been to directly study the products of crystallization of some reactive mixture (gels or glasses) or the component oxides. Normally it is found that over a given P-T range, assemblage A will crystallize and over some adjacent range, assemblage B. A phase boundary is then placed between these regions. The success or failure of this method in establishing equilibrium depends on rates of nucleation, growth and recrystallization being rapid for all phases. These rates are not always rapid compared to the time of experiments and the majority of such studies provide only fields of synthesis. That equilibrium is not established can often be shown by simple analysis of boundary slopes and calculation of entropies of transition. Frequently the slow step is nucleation, less frequently, growth. There is nothing to "tell" a system when the kinetics of these processes must reverse in favor of A or B.

A good example of crystallization in a simple silicate system is provided by the system SiO_2-H_2O. If silica gel or silica glass is crystallized in water in the range 200–500°C at pressures of 500–4000 bars, it is found typically to proceed *via* the following steps:

amorphous → cristobalite → silica − K → quartz

or

amorphous → cristobalite → tridymite → quartz

The phases appear in the inverse order of their stability, a phenomena of most frequent occurrence. The rate of formation of the stable modification, quartz, is extremely sensitive to pressure, rather insensitive to temperature, and at 230°C proportional to $[OH^-]$ and at 330°C proportional to $[OH^-]^2$. In pure water at 300°C and at the vapor pressure of the liquid, the time to establish equilibrium is many years. Nucleation rates are thus no reflection of thermodynamic stability (*16*).

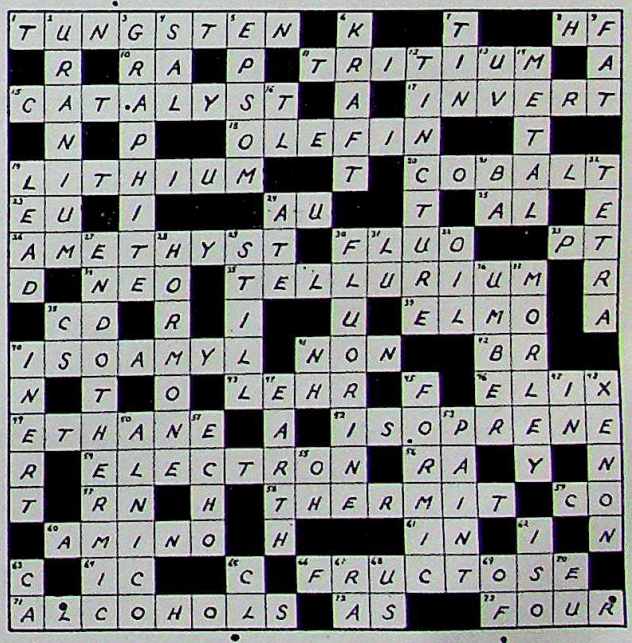
The nucleation barrier can be bypassed by using a mixture of all possible phases in a crystalline state as a starting material and observing the disappearance of all except one possible assemblage. This is a most successful method in many cases. Polymorphic transitions have been fixed with an uncertainty of a few degrees. This often implies a fix on the free energies to within 10 cal or less, an accuracy rarely attainable calorimetrically with silicates. In the MgO–H_2O system, the equilibrium temperature at 1000 bars has been fixed with a precision of ±10° (*17*), again a value superior to that obtainable from the calorimeter. It appears that for these types of processes a combination—direct experiment over a limited range to fix free energies and heat capacity studies to estimate entropies—may provide the most satisfactory thermodynamic data. Where rates of recrystallization are prohibitively sluggish, solubility measurements may be useful. For example, the three polymorphs of Al_2SiO_5 and the related species mullite, $Al_6Si_2O_{13}$, exhibit sluggish nucleation and growth. But the large solubilities of the phases in molten cryolite (*14*) are easily measured and provide unambiguous information on relative stability.

At the present time we have a reasonable outline of the variables significant in geological processes and the range of behavior of mineral systems. While refinement of these data will occur continuously, new developments must include extension of 25°C aqueous physical chemistry to temperatures of at least 1000°C. This extension will require and cause closer ties between geology and chemistry.

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Solution to the Puzzle on p. 268 of the May Issue.



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BOOK REVIEWS

Chemistry Problems

Joseph F. Castka, C. W. Post College, Long Island University, Long Island, New York. Holt, Rinehart and Winston, Inc., New York, 1962. viii + 568 pp. Figs. and tables. 15.5 × 23.5 cm. Paperbound. $3.20.

Stimulating textbooks, as well as able and dedicated teachers, are essential parts of an excellent high school science program. Much good has come from the two NSF-supported group efforts in textbook preparation. But it would be most unfortunate if these texts should discourage individual authorship in this field. The book under review is the product of such individual effort.

The one major criticism of this book is that the author does not, in the first half, even begin to make use of the theory he so ably presents in the latter. Again and again ideas are presented in the Arrhenius and pre-Arrhenius language. Equations are written that bear little resemblance either to modern theoretical ideas or to the composition of the substances involved. For example, the reaction between aluminum and hydrochloric acid is written "2A1 + 6HCl → 2AlCl$_3$ + 3H$_2$." The problem is to calculate "How many grams of aluminum chloride are produced when 72 grams of hydrogen chloride in the form of dilute acid are reacted with excess aluminum?" There is some very important chemistry associated with the fact that AlCl$_3$ (or, rather, Al$_2$Cl$_6$) is *not* obtained under the conditions described in this problem. Mass number and atomic mass are treated as if they are identical, and later defined correctly, just as significant figures are first ignored and then explained. The worst feature is the treatment of solutions of electrolytes. On page 100 there is a table of the equilibrium "process of dissociation or ionization of electrolytes." An example is:

$$NaCl \leftrightharpoons Na^+ + Cl^-$$

The book is divided into six units. Unit One consists of one short chapter, entitled Problem Solving and Science. The chief illustrative problem is The Story of Aspirin. Unit Two, entitled Fundamentals, contains some useful material on the metric system, the use of the slide rule and logarithms, nuclear reactions, oxidation-reduction reactions, and protolysis reactions. It also contains much that is useless and confusing. Unit Three is the usual elementary treatment of gas law problems, and of molecular weight determination by the gas density method and by boiling point elevation and freezing point depression. Unit Four treats concentration of solutions, equilibrium in solution, titration, *p*H, K_{sp}, chemical equivalents, and Faraday's laws.

It is in Unit Five, on chemical bonding and crystal structure, that the author's enthusiasm and ingenuity are made manifest. This long section (182 pages) is the redeeming feature of the book. The language is clear and concise and the problems truly fascinating. Two illustrative problems: (1) describe the hybridization and geometry of the nickel carbonyl molecule (p. 370); (2) calculate, by use of simple geometry, the smallest cation-anion radius ration for cubic body centered crystals (p. 406). Enough of these problems are solved to prevent the able student from giving up before he starts.

Unit Six is entitled Preparation for Examinations and Contests. Sample questions from recent Westinghouse and Advanced Placement examinations are given, although official answers to the latter are not published. The reader is impressed by the wide variation in the quality of questions on each of these examinations.

Although many misprints and small errors were noticed, there are fewer than are usually seen in a first edition of such a comprehensive text. These errors seldom confuse the good student.

The objections to this book, although serious, are objections that apply to practically all high school texts and many college texts in general chemistry. Unit Five is a real contribution to the intellectual ferment that should bring about much less confusing textual material for beginning chemistry courses.

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Physical Organic Chemistry

Jack Hine, Georgia Institute of Technology, Atlanta. 2nd ed. McGraw-Hill Book Co., Inc., 1962. x + 552 pp. Figs. and tables. 16 × 24 cm. $11.50.

This second edition of a popular reaction mechanisms text retains all the many good features of its predecessor. (For review of earlier edition, see THIS JOURNAL, **35**, 368 [1958].) Besides a general updating of most of the text to include significant research appearing since publication of the first edition, there are five major changes in its basic organization. These are:

Addition of problems at the end of each chapter. This is very welcome.

Expansion of the material on methylenes (or carbenes) into a separate chapter, which, as might be expected from Dr. Hine's research interests in this area, is excellent.

Expansion of the chapter dealing with the application of kinetics to reaction mechanisms studies. Since the brevity of this chapter in the first edition was the book's weakest point, this is all to the good. However, this reviewer wishes the kinetics chapter had been expanded still further, and in particular, that another chapter outlining the important *non-kinetic* tools of the physical-organic chemist's trade had also been included. See, for example, Chapter 5 in Gould's "Mechanism and Structure in Organic Chemistry."

Creation of a separate chapter dealing with quantitative correlation of reaction rates and equilibria, principally the Hammett and Taft equations. This chapter is generally well done, except that most students will find the first few pages rather heavy going.

Shifting the chapter on acid-base catalysis to an earlier point in the book. (One might note that this chapter is up-to-date enough to include reference to Bunnett's *w* values papers, even though these were not published until the end of 1961!)

Reviewed in This Issue

Joseph F. Castka, Chemistry Problems
Jack Hine, Physical Organic Chemistry
Keith M. Seymour, Introduction to Organic Chemistry
H. V. Malmstadt and *C. G. Enke*, assisted by *E. C. Toren, Jr.*, Electronics for Scientists: Principles and Experiments for Those Who Use Instruments
W. Brügel, translated by *A. R. Katritzky* and *A. J. D. Katritzky*, An Introduction to Infrared Spectroscopy
Richard Ernst and *Ingeborg Ernst von Morgenstern*, Fachwörterbuch der Chemie: Einschliesslich Verfahrenstechnik und den Grundlagen der verwandten Wissenschaften (Dictionary of Chemistry Including Chemical Engineering and Fundamentals of Allied Sciences), Volume 1, German English
Jean Fouchier and *Fernand Billet*, Dictionnaire de Chimie: Fachwörterbuch der Chemie: Chemical Dictionary
Maurice P. Crosland, Historical Studies in the Language of Chemistry
A. H. Beckett and *J. B. Stenlake*, Practical Pharmaceutical Chemistry: Quantitative Analysis
Anselm E. Strauss et al., The Professional Scientist: A Study of American Chemists
Milos Hudlický, Chemistry of Organic Fluorine Compounds

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As noted earlier, the text generally has been revised to include discussion of or at least some reference to much of the important research in reaction mechanisms published since the appearance of the first edition. To be sure, one can find some significant work which has been omitted. One example is Ingold's paper (*J. Chem. Soc.*, 4054 [1960]) on inductive *vs.* steric effects as the controlling factor in determining the direction of E2 eliminations of onium salts, which one might have expected to see mentioned in Chapter 8. Another is the very limited mention (p. 155) given to Winstein's studies of special salt effects in solvolysis reactions. However, when one considers the ever-increasing volume of physical-organic literature and the need to keep the book to a reasonable size, some such omissions were doubtless inevitable.

All told, this edition represents a significant updating of the original, and because of the rapid pace of research in reaction mechanisms, its purchase to replace volumes of the first edition now in personal or institutional libraries seems indicated.

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Introduction to Organic Chemistry

Keith M. Seymour, Butler University, Indianapolis, Indiana. Prentice-Hall, Inc., Englewood Cliffs, New Jersey, 1963. xiv + 529 pp. Figs. and tables. 16 × 23.5 cm. $9.75.

(This text consists of the author's Organic Chemistry [THIS JOURNAL, 38, 482 (1961)] to which fourteen chapters have been appended. The original thirty chapters, forming the first 311 pages of the book, are printed from the 1961 plates; the errors noted in the cited review have not been corrected.)

The purpose of the added material is evidently to make the text usable for a course in which the non-chemistry majors take only the first semester. Chapters 31 through 33, which deal with molecular orbital theory and rate-equilibrium considerations, are followed by two chapters discussing mechanisms of hydrocarbon reactions and two covering carbonyl compounds in more detail than in the first portion of the book. Chapters on phenols and quinones, naphthalene, polycyclics, heterocyclics, stereochemistry, and finally, polymers and polymerization complete the text.

There are no questions after the rate-equilibrium chapter but the other new chapters have good to excellent (carbonyls, stereochemistry) exercises in problem solving.

Seymour's format—a moderate length survey, followed by a more advanced presentation of a few topics within the same covers—may well meet a real need. In such a treatment, the manner of presentation and choice of material is more critical than in a conventional textbook of organic chemistry. (Seymour's *order* of topics within his two parts is relatively conventional.) Despite wise selection at many points, the author seems to exhibit considerable unevenness in the level of his discussions. Two brief examples: His treatment of free radical oxidation of alkanes is about as extensive as Cram and Hammond's (albeit without *any* mention of hydroperoxides!), whereas the importance of the transition state in the addition of electrophiles to alkenes appears only in a two line footnote. In the first part of the book, ten pages are devoted to color and dyes, but only six to lipids; such a choice of emphasis does not seem consonant with an attempt to meet the needs of biological science majors.

Despite this unevenness and some slips, Seymour's book warrants serious consideration by many instructors because of his different approach to a common problem.

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Electronics for Scientists: Principles and Experiments for Those Who Use Instruments

H. V. Malmstadt, University of Illinois, Urbana, and *C. G. Enke*, Princeton University, Princeton, New Jersey, with the assistance of *E. C. Toren, Jr.*, Duke University, Durham, North Carolina. W. A. Benjamin, Inc., New York, 1962. xi + 619 pp. Figs. and tables. 15.5 × 23.5 cm. $10.75.

In recent years as workers in diverse areas of the experimental sciences have directed their efforts to the solution of increasingly difficult problems involving, for example, the accurate measurement and control of smaller quantities or the measurement of phenomena occurring in shorter times there has occurred an escalation in the availability and use of scientific instrumentation. Much of this is constructed around a compounding of a fairly limited number of easily understood circuits involving diodes, triodes, or transistors.

In the reviewer's opinion, "Electronics for Scientists" is commendable in its attempt to dispel much of the fuzzy thinking and many of the half-truths which those of us without formal training in the subject of electronics have tended to accumulate over the years. The style is clean and comfortable to read, and the authors have avoided almost entirely the jargon of specialized mathematics usually associated with rigorous descriptions of electronic circuits. The book is the outgrowth of an electronics course which the authors have developed over the past several years in the Summer School of the University of Illinois. As such, its format is a hybridization of text and laboratory manual with problems and laboratory exercises following each chapter.

The chapter arrangement of topics presents a discussion which increases somewhat gradually in degree of sophistication. However, the authors commence the book on the assumption that many elementary electronic principles are already familiar in detail to the reader or quickly remembered, and these are placed in two supplements at the end. Since these supplements in large part are fundamental to much of what is discussed throughout the book, their location somewhere at the beginning would have rendered a great service.

Chapter 2 presents a good discussion of power supplies and rectification with attention paid to such practical matters as the color coding of transformer output leads, various types of filtering (single and multiple L-sections, π-Sections, etc.). On pages 72–3 one finds an excellent tabulated summary of schematic filter sections with equations for ripple factors.

Chapter 3 introduces the triode as an amplification device and discusses its behavior and interprets its characteristics in terms of a 12AU7 twin triode. A few words are included to describe circuits involving the triode in terms of a voltage-source equivalent circuit (p. 107 *et seq.*). The principle of the transistor is discussed here rather briefly and in a manner leaving something to be desired. Many examples of common circuits employing transistors are presented from Chapter 3 on.

Chapter 4 follows with a generally good discussion of specific amplifying circuits including a treatment of modes of coupling, decoupling, frequency response, phase distortion and its relation to oscillation, etc. The rather important topic of impedance matching is treated only summarily, however. Voltage and current feedback and tuned amplification are discussed here also. The discussion of feedback is expanded in Chapter 5, where oscillators are treated. Here, in addition, one also learns how the neon bulb, thyratron, and tunnel diode function.

Chapter 6 is a discussion of comparison methods in the measurement of voltages, currents and impedances, and some useful insights are presented for the selection of instruments. An impressive discussion of various impedance bridge circuits is given, and here, for the first time one meets the mysterious "j" notation used to manipulate complex impedances. The reader is referred to Supplement 3 at the back of the book where an explanation is given.

Servo systems are covered in Chapter 7 which precede a discussion of operational amplifiers in Chapter 8. The latter discussion will be of great value to all scientific workers concerned with instrumentation and certainly to electrochemists and electroanalytical chemists.

The last chapter, Chapter 9, is entitled Switching and Timing and Digital Counting Systems. Principles of coincidence and anticoincidence circuits are briefly described. Chapter 9 deals principally with circuits designed to generate and control non-sinusoidal periodic signals. Shaping circuits for these signals are discussed, including diode clipping, clamping, slicing, as well as astable and bistable vibrators including the Schmitt Trigger.

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The laboratory exercises are oriented to a special set of instrumentation (described in Supplement 1) designed by the authors in collaboration with the Heath Company, Benton Harbor, Michigan, and readily available from that manufacturer. It would seem to the reviewer that the many exercises employing this special apparatus could have been segregated to a supplementary working manual. This is a minor point, however, and does not detract from the general usefulness of the textual material which, in the reviewer's opinion, is a highly recommended compilation and working guide to the many electronic circuits frequently encountered in the laboratory.

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An Introduction to Infrared Spectroscopy

W. Brügel, Badische Anilin- und Soda-Fabrik AG., Ludwigshafen a.Rh., Western Germany. Translated from the German Original by *A. R. Katritzky*, Churchill College, Cambridge, England, and *A. J. D. Katritzky*. John Wiley and Sons, Inc., New York, 1962. xv + 419 pp. Figs. and tables. 16 × 24 cm. $9.

It is curious that, in spite of the popularity of the subject, there has been for years no general English-language textbook on the theory and application of molecular or infrared spectroscopy—and then the year 1962 brings us three, viz.: an introduction to the theory, but not the practice, of molecular spectroscopy by G. M. Barrow, J. Chem. Educ., 40, A56 (1963); a textbook emphasizing the practice and application of absorption spectroscopy by R. P. Bauman; and Brügel's book in English translation, covering both theory and application. Brügel limits himself to rotation and vibration spectra, while Barrow and Bauman include electronic spectra.

The intent of the three authors is basically the same—to provide an introduction to the field for the worker with little or no previous background and to enable him to make use of more advanced and more specialized monographs and the current literature.

Part One of Brügel's book, on vibrations and rotations of small molecules, is basically an abstract of corresponding sections of Herzberg's well-known, two-volume "Molecular Spectra and Molecular Structure," even containing many of the same figures. Like most abstracts, it captures the essence of the original, but does not present this material in a more graphic and more easily visualizable fashion—which should be expected from an introductory text.

Part Two embraces succinctly the basic elements of instrumentation and of sample handling. The copious references to current-literature articles should prove quite helpful.

Also included is a well-illustrated chapter on "currently" available commercial instruments. Even though it is useful to describe some representative spectrometers in detail—in order to illustrate the functions of components and to permit a discussion of the interactions that various components may have on each other, i.e., a treatment of the spectrometer as a "system" (for example, the trade-offs between slit width, scanning speed, noise level, costs, etc.)—this reviewer feels that an attempt in a textbook to provide a guide to current instrumentation simply accelerates its obsolescence. In view of the fast-growing field of instrumentation, such tasks are better left to the current literature.

In Part Three, the chapters on group frequencies and qualitative analysis are quite sketchy, but quantitative analysis is handled in a rather scholarly fashion, with considerable depth. A fourth chapter deals with reflection and polarization measurements and, briefly, with microtechniques.

Part Four discusses some specific group-frequency applications, mostly to organic compounds, including high polymers. The last chapter very briefly presents some assorted topics, among them hydrogen bonds, rotational isomerization, thermodynamic calculations, etc.

Brügel's book is neither a how-to-do-it manual nor an easily readable introduction that provides the novice with much feel for the subject. It is, however, a valuable bird's-eye view of the field and has abundant references to guide further study.

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Fachwörterbuch der Chemie: Einschliesslich Verfahrenstechnik und den Grundlagen der verwandten Wissenschaften (Dictionary of Chemistry including Chemical Engineering and Fundamentals of Allied Sciences) Volume 1, German-English

Richard Ernst and *Ingeborg Ernst von Morgenstern*. Brandstetter Verlag, Wiesbaden, West Germany, 1961. 727 pp. 12 × 19 cm. $10.

Dictionnaire de Chimie: Fachwörterbuch der Chemie: Chemical Dictionary

Jean Fouchier and *Fernand Billet*. 2nd ed. Netherlands University Press, The Hague, 1961. 472 + 370 pp. + 429 pp.

In addition to their common purpose of linguistic aid to chemists, these two dictionaries have some other characteristics. It is plain that the compilers were not native to English, and learned it from British sources. Both make some allowance for differences between British and American terminology or spelling. They give much attention to applied chemistry, even into the chemical process industries where some terms have no obvious relation to chemistry. This encourages the trend away from narrow "pure chemistry" dictionaries, a trend in which the first (1953) edition of Fouchier-Billet lays just claim to leadership. Both dictionaries are liberal in entering synonyms under terms, but are notably less liberal about entering the synonyms in their proper alphabetic places.

There are also notable differences beyond the respective bilingual and trilingual characters. The Ernst dictionary (familiarly so-called because Dr. Ernst has compiled a series of specialty dictionaries of which this one is not a part) has considerably the larger vocabulary, about 45,000 terms. It suffers somewhat more from the infection, so difficult to avoid even among professional translators, of too-literal rendition into English. No loss in clarity has been observed from this minor defect, and a compensating feature is that Ernst exposes himself more to this risk by giving more detail in many of his definitions. Ernst is not quite as meticulous as Fouchier-Billet in chemical nomenclature, especially in that Ernst concedes more than seems needful to old terminology, such as sulfuret for sulfide.

Simply as a German-English vocabulary, Ernst is clearly superior; but Ernst's Volume II (English-German) must be included for a comparison with Fouchier-Billet. This leaves to the trilingual dictionary the advantage of a French-English and English-French dictionary in the same volume, with the disadvantage of having a smaller vocabulary. A particular merit of Fouchier-Billet is the liberal use of chemical formulas to illustrate names, often with space-consuming but helpful structures indicated. Misprints are uncommon throughout; without any actual comparison, they seem to occur a bit more frequently in the trilingual dictionary, where the hazards are greater.

Captious criticisms aside, both dictionaries are substantial contributions to interlingual chemical lexicography and each serves well its objective as set forth in its introduction. Chemists interested only in help with German literature will prefer Ernst for its larger vocabulary; those interested in both languages (French and German) can be well content with the new Fouchier-Billet unless their vocabulary needs are unusually extensive.

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Historical Studies in the Language of Chemistry

Maurice P. Crosland. Harvard University Press, Cambridge, Massachusetts, 1962. xvii + 406 pp. Figures. 15 × 22 cm. $9.

The great Lavoisier wrote in 1789 of the "impossibility of isolating the nomenclature from the science and the science from the nomenclature . . . . All physical science is necessarily formed of three

(*Continued on page A468*)

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New Publications

Introduction to Modern Biochemistry

By P. KARLSON

April 1963, 434 pp., $10.00

The work synthesizes the vast knowledge gained in recent years in such fields of research as molecular biology; the chemistry of vitamins and hormones; the constitution and mechanism of action of enzymes; metabolism; and the production, conversion, and utilization of energy. The information is presented in a clear and concise manner, and the most modern viewpoint is employed wherever sufficient evidence substantiates it. The examples and illustrations are particularly suited for teaching purposes, and the inclusion of a large folding chart on metabolic pathways will also help make this work an invaluable teaching guide.

Molecular Genetics

Edited by J. HERBERT TAYLOR

Volume 4 of **Molecular Biology**
An International Series of Monographs
Edited by NATHAN O. KAPLAN and HAROLD A. SCHERAGA

Part 1, 1963, 544 pp., $14.50

This work reflects the current expansion of genetics to include a molecular view of the mechanisms of heredity. In addition to its function as an up-to-date reference work, a major aim of this treatise is to indicate the scope and direction of present and future research.

Enzyme Histochemistry

and Its Application in the Study of Neoplasms

By M. S. BURSTONE

January 1963, 621 pp., $22.50

A comprehensive and up-to-date account of the development and application of microscopic enzyme histochemistry, with particular reference to the application of histochemical techniques in the study of neoplasms. As an integral part of each chapter, two appendixes are included, one dealing with the laboratory organic synthesis of potential substrates, and the other dealing with specific laboratory techniques.

Analytical Microbiology

Edited by F. KAVANAGH

March 1963, 707 pp., $22.00

This important book presents the theory and practice of the use of microorganisms as analytical reagents in assays for antibiotics, amino acids, and vitamins. It contains an up-to-date account of automation as applied to microbiol assaying.

The Chemistry of Nucleosides and Nucleotides

By A. M. MICHELSON

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This volume presents the first detailed account of the general chemistry of nucleosides and nucleotides and their major derivatives, the nucleotide coenzymes and nucleic acids.

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By J. L. WEBB

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Edited by R. M. HOCHSTER and J. H. QUASTEL

Volume 1, June 1963, 669 pp., regular price $26.00
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Design and Function at the Threshold of Life: The Viruses

By HEINZ FRAENKEL-CONRAT

July 1962, 144 pp., paperbound, $1.95

This book is devoted to a description of the chemical make-up and the biological role of the proteins and nucleic acids, the key substances for the functioning of living systems.

Newer Methods of Preparative Organic Chemistry

Edited by W. FOERST

Translated from the German by F. K. KIRCHNER

Volume 2, May 1963, about 400 pp.

This book reflects the wide experience that the authors have had in their respective fields, and the theory, applications, and laboratory procedures that are included within the text will be of interest to all workers in synthetic organic chemistry, pharmaceutical chemistry, and biochemistry.

Colloidal Surfactants

Some Physicochemical Properties

By K. SHINODA, T. NAKAGAWA, B. TAMAMUSHI, and T. ISEMURA

April 1963, 312 pp., $11.50

This work will be of interest to all workers engaged in research or applications concerned with surface active agents in chemistry, biochemistry, biology, or medicine. No other book gives such complete coverage of the solution of purified nonionic agents.

New Serial Publications

Progress in Nucleic Acid Research

An International Series

Edited by J. N. DAVIDSON and WALDO E. COHN

Volume 1, May 1963, 424 pp., $13.00

This new serial publication, which reflects the rapid day-to-day progress in the field of nucleic acid research, presents much more than the standard "Review" of recent literature. It provides a medium for the presentation of new theories and techniques, discussions of controversial material, and publication of timely and significant advances in the field.

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Edited by V. GOLD

Volume 1, April 1963, 443 pp., $13.00

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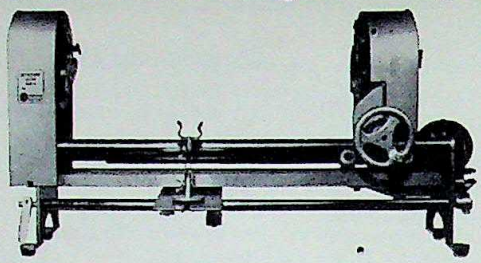
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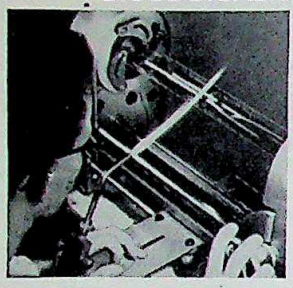
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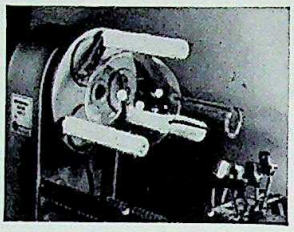


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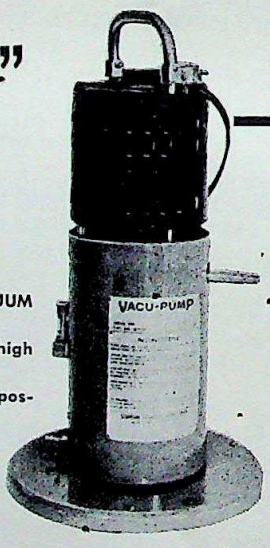
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BOOK REVIEWS

things; the series of facts which constitute the science; the ideas which recall them; the words which represent them." A history of chemical language can provide a significant portion of the history of chemistry itself, and M. P. Crosland in this book has provided historians of science with a well-written and long needed study. At the same time the book will be of interest to the practicing chemist and educator. The problems of systematic nomenclature are still with us today, and this excellent survey of similar if simpler difficulties of the past provides much illuminating reading.

The book is divided into five parts, the central one devoted to the development and acceptance of the first systematic nomenclature of 1787. It was this new system which inseparably accompanied and in part made possible the chemical revolution of Lavoisier and his contemporaries.

Earlier sections are concerned with the language of alchemy, and early chemical terminology. Characteristically, alchemical terms were as often designed for secrecy as for information. Although the seventeenth and eighteenth centuries saw an end to deliberate obscurities, no systematic method appeared in the absence of a viable system of chemistry itself. Prior to 1787, names of substances were often arbitrary and generally gave no hint of composition. Several names for the same substances were in simultaneous use, and the same name was sometimes used for entirely different materials. Our modern nomenclature for inorganic chemistry derives directly from the new system of 1787 built on the principle that a name ought to express composition.

There is a fourth section on chemical symbolism, beginning with the astrologically based symbols of alchemy, and ending with the introduction of modern literal ones by Berzelius about 1815. This section thus complements the much earlier book (1928) of Caven and Cranston "Symbols and Formulae in Chemistry" which is chiefly concerned with the topic after Berzelius. The final section of Crosland's book is devoted to the language of organic chemistry, concluding with a brief account of the Geneva Congress of 1892.

As a survey of a large topic, the book does not contain as much anecdotal material as a general reader might like. Nor does the broad scope allow the author to analyze the chemical problems behind the changing nomenclature as thoroughly as the historian would like. But these limitations do not detract seriously from the interest and usefulness of the book as written. Rather they emphasize the need for smaller but more intensive studies in this area, for which this book will provide the background. The utility of the book is further enhanced by the extensive indices of both proper and chemical names.

ROBERT SIEGFRIED
University of Illinois
Urbana

(*Continued on page A470*)

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Graduate Level Textbooks in Chemical Research and Teaching —New and Forthcoming from McGraw-Hill

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By LOUIS HARRIS and ARTHUR L. LOEB, both of Massachusetts Institute of Technology. Available in June, 1963.

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HEAT TRANSFER

By JACK P. HOLMAN, Southern Methodist University. Off press.

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MASS SPECTROMETRY

Edited by C. A. McDOWELL, University of British Columbia. McGraw-Hill Series in Advanced Chemistry. Available in August, 1963.

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BOOK REVIEWS

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The Professional Scientist: A Study of American Chemists

Anselm L. Strauss and *Lee Rainwater* with *Marc J. Swartz* and *Barbara G. Berger*. Aldine Publishing Co., Chicago, 1962. xiv + 282 pp. 15 × 21.5 cm. $6.

This book provides a good picture of the thinking of approximately 3000 American chemists in relation to the three facets of chemistry. The first might be called the chemist and his work. This touches on a wide variety of subjects such as how chemists become chemists, types of careers of chemists, the chemist's work morale, how others see chemists. The second is the chemist as a professional; here there are questions dealing with chemistry and other professions, chemistry and medicine, chemists and the public, some potential dangers to the profession, and chemists and industrial management. The final facet has to do with the chemist and his professional organization—The ACS; non-members, membership and participation, whether the Society is sufficiently professional, the Society's functions—past and present, who runs it, attitudes toward membership, and symbolic meanings. The book closes with a concluding note on professions.

The qualitative data used to identify the beliefs, ideas, and prejudices of the 3000 chemists came in part from interviews with 200 randomly selected ACS members in 10 cities, 75 non-ACS chemists in Chicago, and 50 businessmen and other professionals. The quantitative data, evaluated via IBM cards, were the results of a questionnaire sent to 2700 male ACS members.

Chapter I entitled Professions and Industrialization: A Framework for the Study, and Chapter XII, A Concluding Note on Professions, provide what might be called background for the data developed by the interviews and the answers to the questionnaire. Here the authors leave the fairly safe field of data summarizing and interpretation for the vagaries of speculation. There are many statements in these chapters which the reviewer questions. Example (p. 7), "The professional schools are putting more emphasis on science in their graduate education as *a result of its prestige in the university*." They are, but not for that reason. Example (p. 220), "Professors in pure-science disciplines typically are *interested in teaching future colleagues, not in turning out personnel for non-academic settings*." This I do not believe. Example (p. 225), "The graduate students (in physics) who enter the aircraft and other industries are scarcely regarded at the great universities as equal to physicists who remain on the campus or join such institutions as Bell Laboratories." How an individual is regarded depends on the individual and not on where he takes a job. There are as good physicists working in industry and government today as there are in the universities.

Example (p. 218), "As long as university departments graduate only those students who follow primarily in the footsteps of their teachers, there is no question of professionalization. The graduate is a scientist, or more accurately, a scientist and a professor" (but apparently not a professional man). Finally (p. 3) "They [the chemists] are also, in response to the needs of an industrializing society, engaged in teaching, administration, and other activities less obviously connected with research. Primarily, however, the profession (of chemistry) is *one of scientific discovery and the practical application of the results to the creation of new products*." This could seemingly exclude the chemist who is concerned with pure scientific research and who has no interest whatever in new products.

Example (p. 29) "Chemistry of all the natural sciences has the highest proportion of men—90%." Physics has approximately 97%. Example (p. 36) "One out of six chemists does his work at an educational institution" while on p. 29 we read that "in 1950 one tenth of the chemists were found on campuses." There is something missing in this comparison—it is probably the number of "chemists" who teach chemistry in high school.

Any quotations from this book should be confined to quantitative data. IBM machines can count—but interpretation and speculation certainly are beyond them.

HARRY F. LEWIS
Institute of Paper Chemistry
Appleton, Wisconsin

(*Continued on page A472*)

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with the cooperation of G. Bombara, I. Epelboin, C. Furlani, S. Gallone, P. Hjerten, M. Lederer, and A. Liberti. First English edition, Translated by P. J. Mill.

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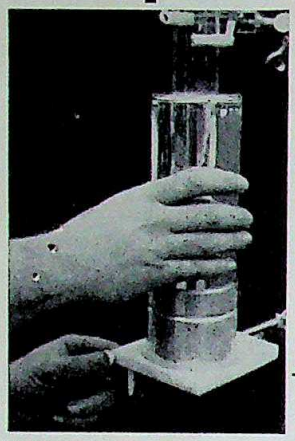
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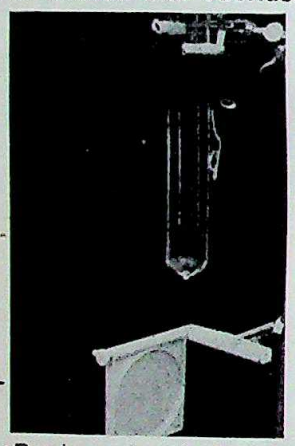
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A. H. Beckett, Chelsea College of Science and Technology, and *J. B. Stenlake*, Royal College of Science and Technology, Glasgow. University of London at the Athone Press, 1962. viii + 378 pp. Figs. and tables 16 × 25.5 cm. $10.10

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N. M. FERGUSON
University of Houston
Houston, Texas

Chemistry of Organic Fluorine Compounds

Milos Hudlický. The Macmillan Co., New York, 1962. 536 pp. Figs. and tables. 17.5 × 24.5 cm. $9.50.

This instructive and inclusive volume, which is the American printing of the recently revised translation of the original work, published in England (1961), con-

(*Continued on page A474*)

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ORGANIC REACTIONS
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Editor-in-Chief: ARTHUR C. COPE. *1963. Approx. 400 pages. Prob.* $12.50.

MEDICINAL CHEMISTRY—Volume VI

Edited by E. E. CAMPAIGNE, *University of Indiana; and the late* W. H. HARTUNG, *formerly of Medical College of Virginia. 1963. Approx. 448 pages. Prob.* $25.00.

COMPLEXATION IN ANALYTICAL CHEMISTRY
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By ANDERS RINGBOM, *Åbo Akademi, Finland.* Volume 16 in the Interscience Chemical Analysis Series. *1963. Approx. 408 pages. Prob.* $15.00.

QUANTUM BIOCHEMISTRY

By BERNARD PULLMAN, *The Sorbonne; and* ALBERTE PULLMAN, *Centre National de la Recherche Scientifique.* An Interscience Book. *1963. 867 pages.* $27.50.

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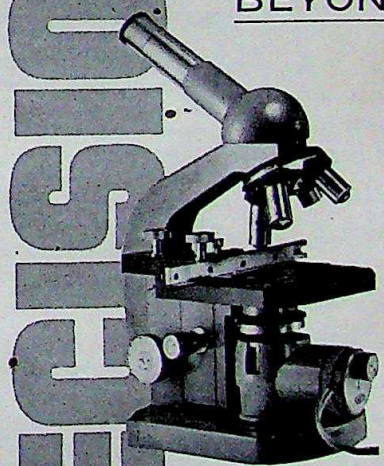
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tains a modern and detailed description of the chemistry of organic fluorine compounds. It is well illustrated by more than seven hundred equations, in many of which yields are indicated, together with over eighty tables, forty drawings, and an equal number of detailed descriptions of pertinent experimental procedures, many of them as carried out by the author himself. In addition, the material is well documented by more than a thousand references to the original literature spread over a wide selection of journals, together with numerous cross references as well.

The three most important chapters dealing with the introduction of fluorine into organic compounds together with the preparation and reactions of these substances take up more than half of the book. There are also minor chapters dealing with apparatus, reagents, properties, analysis, commercial applications and other related subjects. The presentation in this book is clear, thorough and easy to follow. It should be emphasized, however, that the treatment throughout is essentially factual, and that only a modest attempt has been made to deal with the more complex theoretical considerations necessary to explain the marked and characteristic influence of fluorine upon the physical and chemical properties of organic molecules. Presumably this may be a noticeable advantage to those who wish to use the volume for quick and ready reference. Fortunately, only a relatively few minor omissions and typographical errors are to be found in this text.

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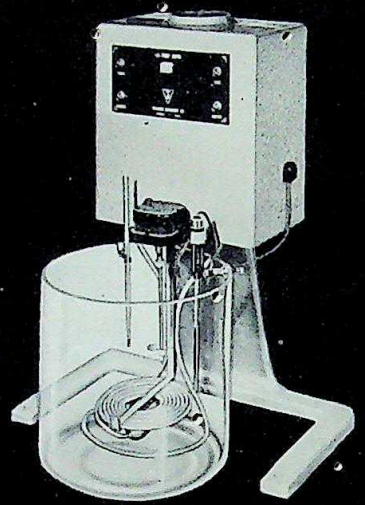
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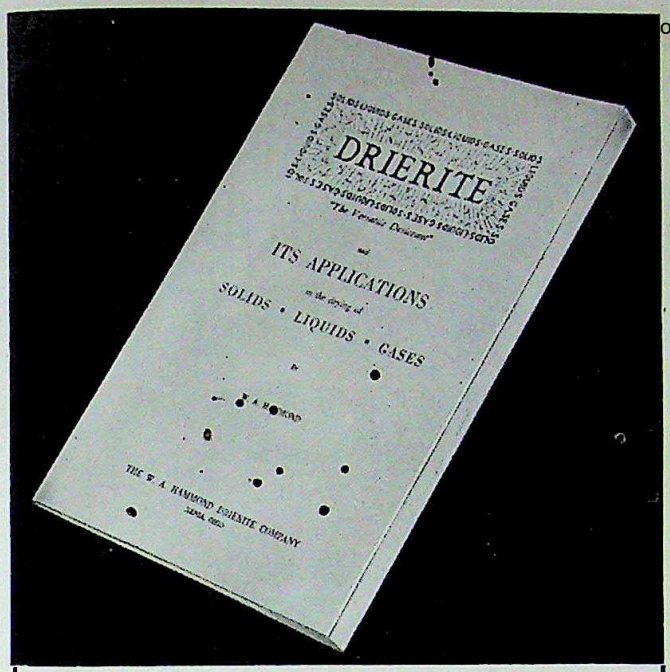
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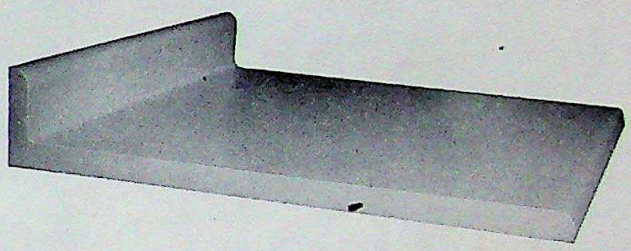
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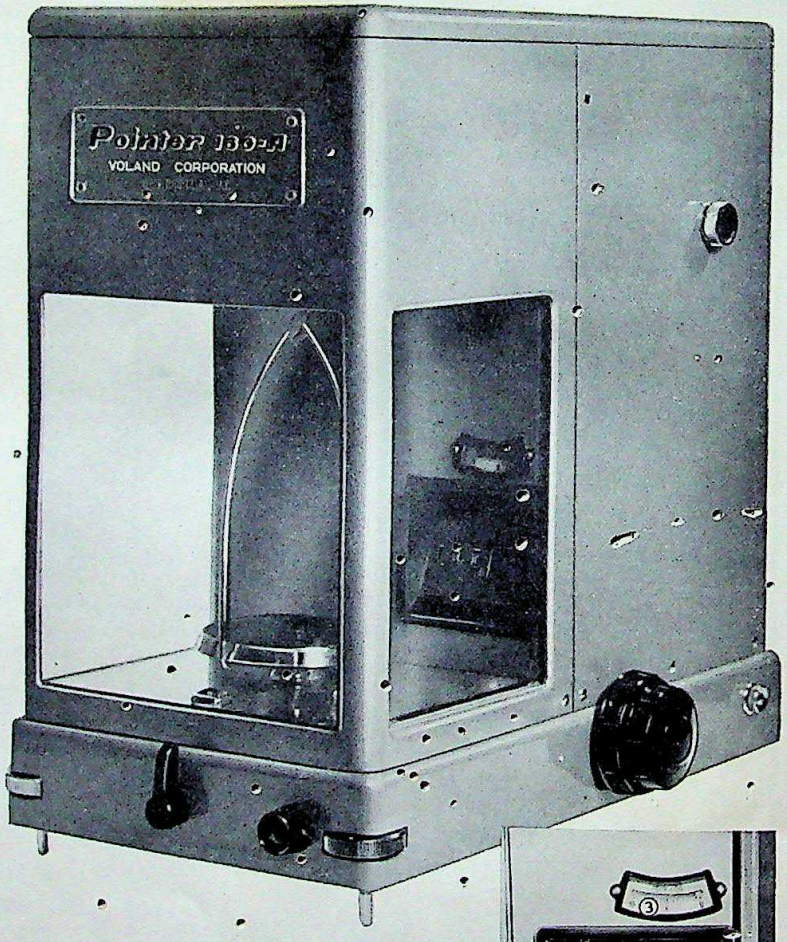
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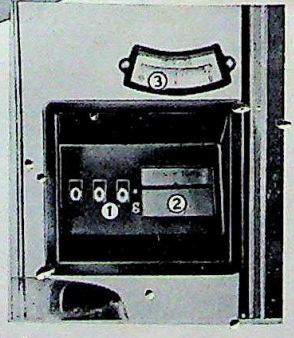
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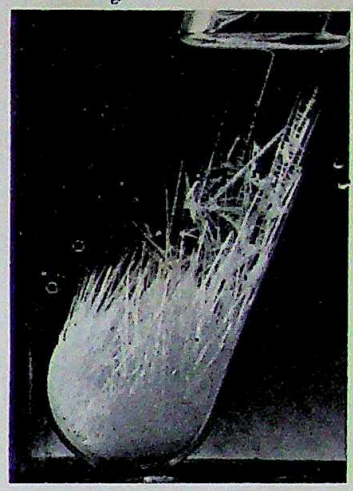
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Sture Skyle, Teachers Training College, Kristianstad, Sweden, suggests the use of turpentine as a solvent for sulfur from which the sulfur may be recrystallized in the prismatic or monoclinic form. Such a solution saturated at the melting point of sulfur will, upon cooling, deposit the sulfur as long needle-like crystals. These grow in prismatic form even below the transition point. Since turpentine can be heated at temperatures above the melting point of sulfur, filtration is not necessary. The undissolved sulfur melts and sinks so that the solution becomes quite transparent. Mixtures of turpentine and kerosene will also serve. The advantages over carbon disulfide in terms of comfort and safety are obvious.



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Professor John E. Benson, Gettysburg College, suggests an elaboration of Dr. Alyea's demonstration ("Tested Demonstrations," 5th ed., JOURNAL OF CHEMICAL EDUCATION, Easton, Pa., 1962, p. 21: 9–7.) on fog formation. A lighted cigarette is held close to the stopcock arm leading to the air. The flask is vented briefly to introduce a small, almost invisible amount of smoke. When the flask is again evacuated, a dense cloud will form.

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OXYGEN IN AIR

An experiment or demonstration that reputedly shows that air is composed of $^1/_5$ oxygen occurs in many texts, manuals, and other publications as follows: "A burning candle is supported in a large, flat dish containing water. A glass bottle or jar is inverted over the candle with the opening below the water level. After the candle is extinguished, water rises in the jar." It is frequently stated that this provides evidence concerning the composition of the air. Dr. Joseph Glanz of 87-81 146th Street, Jamaica 35, New York, points out that if the data corresponds to a loss in volume of 20%, it is due to a fortuitous combination of compensating errors and that the explanations given are usually completely erroneous due to the following factors:

1. When the candle is burning, the gases in the jar are heated well above room temperature and will contract greatly on cooling.
2. There is usually a loss of gas from the system due to the expansion of gases heated by the candle flame.
3. Combustion under these circumstances is incomplete.
4. As oxygen is consumed, carbon dioxide is produced in equal volume.
5. Carbon dioxide is not very soluble in water.

See also JOHN H. ROSENGREN, "Old Experiment—New Twist," *Elementary School Science Bulletin*, National Science Teachers Association, Washington, D. C., Nov. 1962, p. 10, and H. N. ALYEA, "Tested Demonstrations in Chemistry," 5th ed., JOURNAL OF CHEMICAL EDUCATION, Easton, Pa., 1962, p. 18: 2–4.

CHEMILUMINESCENCE IN ELECTROLYSIS

Fidel Villarreal and Octavio García of the Instituto Tecnologico de Monterrey of Monterrey, N. L., México, use the oxidation taking place at the anode in an electrolysis cell in place of hydrogen peroxide in performing the usual chemiluminescence demonstration with luminol (3-aminophthalhydrazide). The usual variations including the addition of ice to emphasize the "cold" aspect of the phenomena and the extinguishing of luminescence by acidifying the solution may be performed in the electrolytic cell as they are with the more conventional demonstration. See H. N. ALYEA, "Tested Demonstrations in Chemistry," 5th ed., JOURNAL OF CHEMICAL EDUCATION, Easton, Pa., 1962, p. 7: 2–14, and also HUNTRESS, E. H., STANLEY, L. N., AND PARKER, A. S., THIS JOURNAL, 11, 143 (1943)

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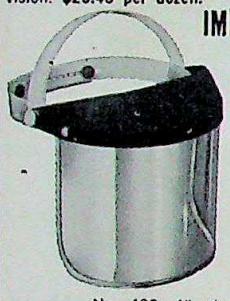
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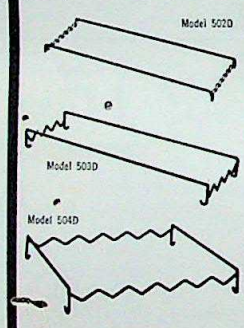


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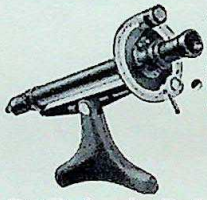
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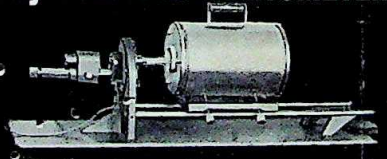
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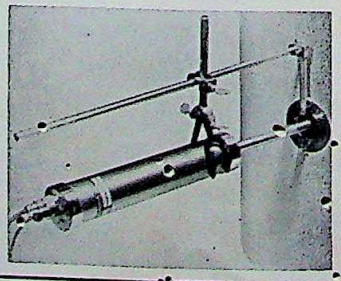
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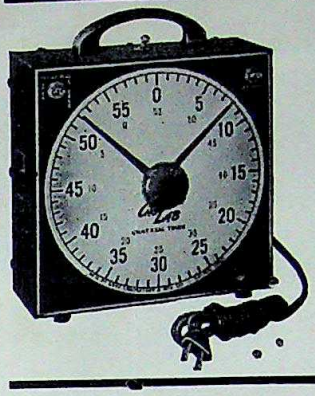


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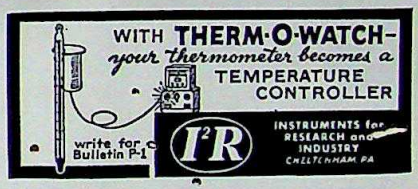


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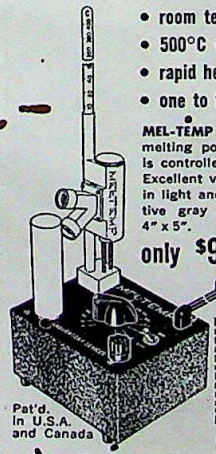
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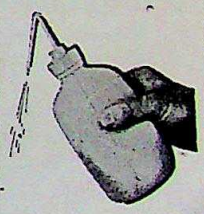
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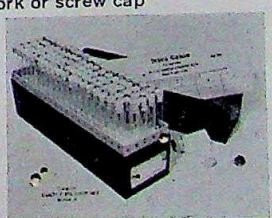
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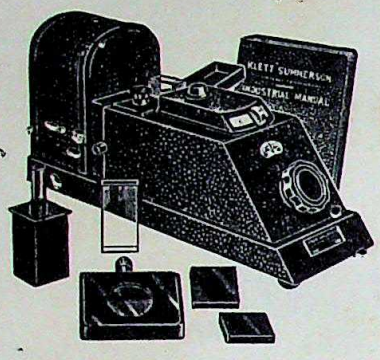
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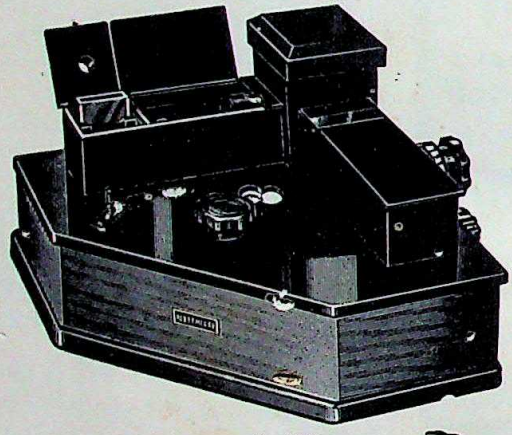
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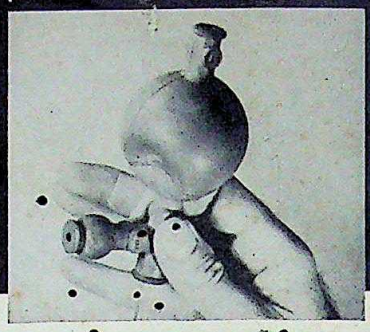
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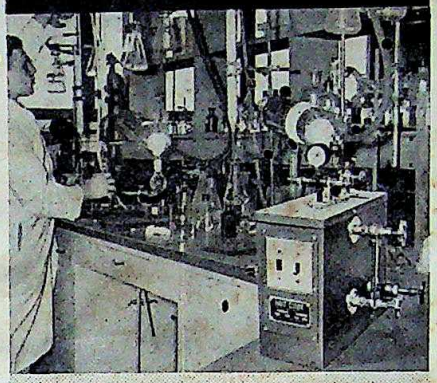
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